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Chemical Progress

Handbook of an Exhibition

1947

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Chemical Progress

Handbook of an Exhibition
held at the
Science Museum
July to September 1947
by
the Chemical Society and the
Department of Scientific
and Industrial Research
as part of the
Centenary Celebrations
of the Chemical Society

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FOREWORD

TO the Joint Exhibition Committee of the Chemical Society and the Eleventh International Congress of Pure and Applied Chemistry fell the task of arranging an Exhibition illustrative of the achievements of British Chemists since the foundation of the Chemical Society in 1841. In addition, the Society has collaborated with the Department of Scientific and Industrial Research which, in association with the Central Office of Information, has arranged a section of the Exhibition illustrating some of the applications of modern chemistry in everyday life.

In several ways this Committee has been fortunate : it has had the willing co-operation of nine Conveners of Panels, illustrative of various aspects of Chemistry, who have supplied texts and have chosen exhibits for their respective sections ; it has had the support of the Director of the Science Museum, Dr. H. Shaw, who has placed at its disposal staff, floor-space and display cases. For compiling the accounts of the various sections into its Catalogue, it has had the assistance of Dr. Sherwood Taylor, and finally it desires to acknowledge the efficient work and enthusiasm of its Secretary, Mr. J. R. Ruck Keene.

As a result, the Committee feels that this Catalogue of this Exhibition is a document of more than passing interest, for it is an authoritative account of the development of chemistry in Britain during the last hundred years and, as such, a handbook for the student of chemistry.

Thanks are due also to the lenders of exhibits, historic and illustrative, too many to enumerate specifically.

ROBERT ROBERTSON,

Chairman, Joint Exhibition Committee

CONTENTS

Section 1

HISTORICAL

Chapter / Page

I The Properties of Gases 1

II The Solid State 6

III Colloid Science and Surface Chemistry 12

IV Liquids and Solutions 15

V Chemical Reactions 21

VI Valency and Atomic Structure 31

VII Inorganic Chemistry 36

VIII Agricultural Chemistry 41

IX Organic Chemistry and Biochemistry 43

X Analytical Chemistry 54

Section 2

CHEMISTRY IN EVERYDAY LIFE 61

by Dr. James Lawrie

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Section 1

HISTORICAL

CHAPTER I

THE PROPERTIES OF GASES

The numerals in brackets, *e.g.* (21), are references to the second part of each chapter wherein the exhibits are described.

THE exhibits in this section illustrate the work of British scientists in the experimental investigation of the properties of gases, excluding work which comes under the headings of Chemical Kinetics, and Analysis. What is left relates mainly to the physical properties of gases ; but chemists have contributed to a considerable extent to our knowledge, and the work of many physicists in this connection is of special interest to chemists. This explanation is offered to account for the fact that the range of the section is very limited.

The diffusion of gases and allied phenomena

The phenomena of mixing of gases were known to Priestley, Dalton, Davy, and probably to many others, before Professor Thomas Graham (1) began the series of researches which extended over the period 1830 to 1845. To use his own words, he distinguished between (1) *Effusion* of gases, by which is meant the passage into a vacuum of a gas through a small aperture in a thin plate ; (2) *Transpiration* of gases, or their passage through tubes of small bore, and of greater or less length ; and (3) *Diffusion* of gases. He studied the latter phenomenon with, and without, porous septa. He found that the Square Root Law applied to diffusion and to effusion, but could not find any connection between rates of transpiration and density of gases, as no such relationship exists.

The work is, of course, of interest to chemists, and particularly for the reason that Graham was the first President of the Chemical Society.

While a great deal of work has been carried out in connection with this subject, particularly of a theoretical character, it is impossible to follow it here. However, reference may be made to the application of a diffusion method (2) by Lord Rayleigh and (Sir) William Ramsay for demonstrating that argon existed in the atmosphere as an individual, and was not a product of the processes by which it was separated.

The rare gases

It may fairly be claimed that the pioneers in this field were British. In 1785 Henry Cavendish showed that air contained one eighty-fifth part of its volume of a gas which could not be made to combine with oxygen, or nitrogen, by passing electric sparks through it (3). In 1892, Lord Rayleigh showed that atmospheric nitrogen was heavier than nitrogen from chemical sources. His attention was called to Cavendish's experiment, which he repeated (4), and found that air certainly contained some gas other than those that were known. In the meantime, Professor W. Ramsay, knowing of the work of Lord Rayleigh on the density of nitrogen, and also of Cavendish's work, had been treating atmospheric nitrogen with hot magnesium (5), and had obtained from it a gas nearly half again as heavy as nitrogen. From this stage, the two investigators worked in collaboration, and early in 1895 they published an account of the discovery of argon (at. wt. 40).

A few weeks later, Ramsay examined the gas given off on heating the Swedish mineral cleveite (6). The spectrum showed a yellow line corresponding with the line observed in the spectrum of the sun's chromosphere by Norman Lockyer in 1868. The gas was found to have an atomic weight of 4, and was named helium.

The facts now suggested to Ramsay that these gases belonged to an eighth group in the Periodic Table, and he commenced a search for the missing elements of the series. In this work he was joined by Morris Travers. No trace of the presence of unknown elements could be found in gases obtained from minerals, meteorites, or mineral springs. In 1898, they returned to the study of atmospheric argon, and found that it consisted mainly of an inactive element of atomic weight 40, but that it also contained small quantities of elements which they named neon (at. wt. 20), krypton (at. wt. 84), and xenon (at. wt. 131). The separation of the gases was effected by liquefaction and fractional distillation, using liquid air, or liquid hydrogen in the case of neon (7).

In 1900, Rutherford and Soddy showed that radioactive substances gave off ' emanations,' which had properties closely similar to those of the rare gases. In 1903, Ramsay and Soddy showed that the disintegration of radon, the emanation from radium, gave rise to helium (8). In 1912, Ramsay and Whytlaw-Gray determined the density of radon by weighing less than a cubic millimetre of the gas (9), the values obtained giving the figure 222 for the atomic weight, which accorded with other known facts.

The liquefaction of gases

In the *Journal of Science and Art* of the year 1824, Michael Faraday reviewed the state of knowledge concerning the liquefaction of gases. Ammonia had certainly been liquefied by de Morveau, as had sulphur dioxide by Monge and Clouet, by cooling alone ; and Northmore had condensed chlorine by compression by means of a pump. The review arose out of his own work, carried out in the Royal Institution at the suggestion of Davy, and published in 1823. He generated gases under pressure in glass tubes, sealed and bent so that the gas could be condensed by cooling (10). In this way he liquefied chlorine, hydrochloric acid, sulphur dioxide, sulphuretted hydrogen, carbon dioxide, nitrous oxide, and cyanogen.

Faraday's more important work was published in 1845. He used two compression pumps, with pistons ½ inch and 1 inch in diameter, operated in series, by means of which he could obtain pressures up to 50 atmospheres, measured by a mercury-air manometer (10). The gases were compressed into capillary glass tubes which could be cooled down to — 100° C. The lowest temperatures were obtained by means of a mixture of solid carbon dioxide and ether, evaporating under reduced pressure under a bell jar, and were measured by an alcohol-thermometer. Series of temperature-pressure relations were recorded for the first time. With this apparatus he succeeded in liquefying all the known gases with the exception of hydrogen, oxygen, nitrogen, nitric oxide, and carbon monoxide.

These gases came to be referred to as *permanent ;* but it is necessary to recall the fact that in 1822 Cagniard Latour had shown that liquids heated to a certain temperature evaporated completely. It remained for Professor Thomas Andrews of Belfast to make, in the 'sixties, the first quantitative investigation of this phenomenon, and to demonstrate the continuity of the gaseous and liquid states, and the existence of the critical temperature (11). His work was extended on the theoretical side by his colleague, Professor James Thomson.

In the interval, the work of Van der Waals extended theory still further, but the next entrant into the experimental field appears to have been J. B. Hannay, of Glasgow (12). He improved the Andrews technique and showed that there was complete continuity in the behaviour of fluids towards solids above and below the critical point. If a solid dissolved in a liquid below the critical point, it did not separate when there was no longer evidence of the presence of liquid. He also showed that the surface-tension of liquids diminished with rise of temperature, and became zero at the critical point.

William Ramsay and Sydney Young commenced their work on liquid-vapour systems at Bristol in 1884. They worked mainly with pure liquid organic compounds, and also with water and with mercury. From the results of their experiments they were able to verify important relationships predicted by James Thomson, Clausius, Van der Waals, and others. A contribution to the experimental study of such problems is their apparatus for maintaining constant temperatures by means of pure liquids boiling at constant temperature. The work led Ramsay to investigate the molecular complexity of liquids by studying the change of surface tension with temperature (13). Young continued the work on *p-v-t* relationships with series of pure liquids, and turned his attention also to problems of separation of liquids by fractional distillation (14). His work is both of scientific and technical interest.

In the late eighties interest in gas-liquid systems centred on work on the liquefaction of the so-called permanent gases, commencing with oxygen. In 1885, Olszewski used an apparatus, working on the cascade principle of Pictet, to produce a small quantity of the liquid. In 1891 (Sir) James Dewar, using a similar apparatus, obtained liquid oxygen at the Royal Institution. In the course of these investigations, Dewar invented the vacuum vessel, or Dewar Flask (15), which will always be regarded as an outstanding contribution to low-temperature research.

In 1895, W. Hampson in England and C. Linde in Germany devised methods for liquefying gases by utilising the Joule-Thomson effect (16). Air at about 150 atmospheres pressure passed through a coil of closely wound small-bore copper pipe, and expanded at a valve at the end of it, the cooled gas returning over the outside of the coil. Cooling was progressive and liquefaction resulted. Hampson, in collaboration with K. S. Murray, of the Brin's Oxygen Co. Ltd. (British Oxygen Co. Ltd.), devised the well-known apparatus which for many years supplied all the liquid air used in research laboratories.

Theory indicated that hydrogen could not be liquefied by the Hampson-Linde process, unless the compressed gas were cooled to a low temperature before entering the regenerator coil. In 1896, Dewar published in the *Journal of the Chemical Society* an account of the liquefaction of hydrogen using an apparatus similar to that of Hampson, but afterwards withdrew the statement. In 1898, he showed liquid hydrogen at the Royal Institution. In 1900, M. W. Travers constructed a simple apparatus on the Hampson principle for producing liquid hydrogen (17), and used the liquid for the separation of neon from helium and argon. It was described in the *Philosophical Magazine* in the following year.

Work at low temperatures in the Royal Institution and in University College, London, was limited by the lowest temperature which could be reached using solid hydrogen, which was about 13° K. The story then reopens in this country with the establishment of cryogenic laboratories in Cambridge and Oxford, and with the use of liquid helium, and of magnetic methods, for the exploration of much lower temperatures. This work lies entirely within the range of physics. However, drawings of the latest design in plant for producing liquid hydrogen (18) and liquid helium (19) are contributed by Professor F. Simon and Dr. F. F. Allen.

High vacua, cathode-rays, etc.

As a pioneer in this field, (Sir) William Crookes carried out work which is remarkable. It commenced in the early 'seventies with the invention of the so-called radiometer (20). He was led to it by the idea that the attraction between masses might be influenced by their temperature. The invention created a great deal of interest, and lively discussion between Crookes, Osborne Reynolds, G. G. Stokes, and Schuster, led to an explanation based upon the kinetic theory which was accepted by all. This seems to have been Crookes' first adventure in the field of high vacua, in which he used the seven-fall Sprengel pump invented by his assistant, Charles Gimmingham. His long series of investigations in the cathode-rays led him into regions, the full exploration of which required knowledge not then existing, but are universally recognised as showing experimental skill of the highest order, and scientific foresight. Some examples of his apparatus are exhibited (20). One particular tube, which has a concave cathode by which the cathode-rays are focused on an inclined platinum plate, was found, after Röntgen's discovery of the X-rays in 1895, to be the effective apparatus for producing them.

Temperature, pressure, volume, and mass relations in gases

The complete story should open with an account of the work of Joule and Thomson (Lord Kelvin) on the temperature change observed in gases when they are allowed to expand freely, carried out just a century ago, and should follow through experimental and theoretical work on thermometry. But this cannot be illustrated by diagrams or apparatus. Work on volume/mass relations is of interest to chemists. That of Lord Rayleigh on the densities of the principal gases introduced a new method of measuring pressures (21). He also showed the importance of correcting the loss of buoyancy of weighing globes owing to contraction on exhaustion. Lord Rayleigh also investigated pv/p relationships from atmospheric pressure to very low pressures. Professor Whytlaw-Gray also carried out extensive investigations on *mass/volume* and pv/p relationships. His work on the application of the micro-balance (p. 2) introduced many new experimental features (22).

EXHIBITS

The Properties of Gases

1. Apparatus used by Thomas Graham in his work on the diffusion of gases, 1829–1845.
2. Rayleigh-Ramsay diffusion apparatus. This consists of the pipe stem atmolyser.
3. The Cavendish experiment. Demonstrating the presence of an inert gas in the atmosphere.
4. Rayleigh's sparking method, described and illustrated in the original paper on argon by Ramsay and Rayleigh.
5. Ramsay's apparatus for preparing argon in quantity (1894).

6. Original spectrum tubes of the inert gases and specimen of cleveite.
7. Apparatus used for separation and purification of the inert gases (Ramsay and Travers, 1898).
8. Original spectrum tubes which contained radium emanation (Ramsay and Soddy, 1903).
9. Ramsay and Whytlaw-Gray micro-balance.
   (Lent by Professor Whytlaw-Gray.)
10. Faraday's liquefaction tubes and pump.
   (Lent by the Royal Institution.)
11. Andrews's apparatus to demonstrate the continuity of the liquid and gaseous state.
12. Hannay's compression and surface tension apparatus.
13. Surface tension apparatus (Ramsay and Shields).
14. Young's apparatus for the fractional distillation of liquids.
15. The development of the vacuum flask.
   (Lent by the Royal Institution.)
16. Hampson air liquefier.
17. Travers's hydrogen liquefier, 1900.
18. Diagram of the hydrogen liquefier developed at Oxford by Simon.
19. Diagram of Kapitza's helium liquefier developed at Cambridge.
20. Crookes's radiometer and cathode-ray tube.
21. Apparatus with which Rayleigh examined the density of nitrogen.
22. Density apparatus developed by Whytlaw-Gray.
   (Lent by Professor Whytlaw-Gray.)

Exhibits Nos. 1–8, 11–13 and 16–17 were arranged by the Chemistry Department of the Science Museum, from exhibits in the collections.

CHAPTER II

THE SOLID STATE

THE history of the progress in our knowledge of solid materials during the last hundred years opens on the frontiers of chemistry and crystallography. The importance of crystals had long been recognised. Whether grown by evaporation of aqueous solutions of various salts or found in more natural conditions as mineral constituents of rocks, crystals, bounded by plane faces and not by curved ones as are animals and plants, announce the regularity of their architecture all through by their outer geometrical form. The realisation that all solid matter except glass is crystalline and that living matter is itself to a greater or less extent crystalline is dependent upon a new technique and its assiduous application during the last thirty years. The story of the solid state is a triumphant extension of the atomic theory.

The early science of crystals was not confined to a study of external symmetry. Robert Hooke had suggested in the seventeenth century that the regularity of form of the tiny quartz crystals lining flint nodules resulted from a close-packing of minute spheres, but it was not until the end of the eighteenth century that the Abbé Haüy reduced the apparent complexity and multiplicity of the shapes of crystals by a simple idea based upon the observed cleavage directions of common minerals. A crystal of calcite, no matter what its external form, *i.e.* habit, whether it be a hexagonal prism with flat ends, whether a rhombohedron or a tapering scalenohedron, always, on fracture, yields cleavage rhombs of constant angle. Rock salt or galena, minerals with cubic cleavage, yield rectangular blocks. Haüy discovered that he could reconstruct the variously shaped crystals of any one mineral by packing together a very large number of the appropriate unit bricks all of the same shape and size. Faces other than those parallel to the cleavages of Haüy's primitive form would have, of course, a step-like appearance and not mirror-like surfaces ; so that Haüy conceived his primitive form as invisible to the eye. In this way he showed how scalenohedra, or other forms of calcite, could be built up from primitive rhombohedra and octahedra of a cubic mineral from primitive cubes. Haüy's theory provides also an elegant explanation of the law of rational indices and as will become apparent can readily be translated into the modern theory of crystal structure (27).

The problem of crystalline form was also attacked from a purely geometrical point of view with no reference to primitive forms or theory of structure. Romé de l'Isle's discoveries, made like Haüy's at the end of the eighteenth century, of the constancy of interfacial angles of crystals of the same substance and of the interrelation of different crystal forms provided the impetus for a systematic study of crystal form. Wollaston in 1809 invented the first reflecting goniometer (23), so giving crystallographers the accurate tool they needed for classifying crystals of known substances into the seven systems of symmetry, and we owe to Brewster's optical researches the first correlation of isotropic, uniaxial and biaxial characters of crystals with their external symmetry. Systems of notation to express the directions of each crystal face relative to the coordinate axes of references were devised, and of these Miller's, for simplicity and ease in calculation, has alone stood the test of time. The time was ripe for the discovery, actually made by Hessell in 1830, but overlooked for sixty years, of the limitation of crystal symmetry to thirty-two types, the so-called thirty-two point-groups or symmetry classes.

By 1841 crystallography had been established as a science for half a century, and some fundamental discoveries already connected crystalline form and chemical constitution. Dimorphous forms, *e.g.* rhombohedral calcite and orthorhombic aragonite, the orthorhombic and monoclinic forms of sulphur had been recognised and the difference in form had been shown to exist without any difference, however slight, in chemical composition. Mitscherlich had not only established dimorphism for artificial crystals, but also discovered series of artificial salts of essentially different chemical composition with the same crystal symmetry, a relationship termed isomorphism. He, therefore, inferred that the crystalline form of a chemical compound depends not only upon its composition, but also on the configuration of the atomic groups.

The middle of the nineteenth century marked advances on all fronts of the solid state. Haüy's conception led directly to the idea of a space lattice and to the question of how many ways of partitioning space are possible ones. Bravais' fourteen space lattices published in 1850 provided the essential framework for Fedorov, Schoenflies and Barlow, who each independently and by different methods deduced the now familiar 230 space groups (26). Each space group results from placing one of the thirty-two point-groups of symmetry elements at each of the points of a Bravais lattice infinitely extended. Thus the scaffolding for all formal crystal structure analysis was ready just before the discovery of X-rays in 1895.

During the same period Pasteur had separated right- and left-handed crystals of the sodium ammonium salt of racemic tartaric acid and shown that solutions of each kind had equal and opposite rotatory powers on the plane of polarisation of light. This achievement led eventually to the idea of the spatial distribution of the four valencies of carbon at the angles of a regular tetrahedron instead of arrangement in a plane. Thus the possibility of three-dimensional mirror-image formulæ and the fruitful concept of stereoisomerism came into being. From then to the end of the century the syntheses of myriads of organic compounds of relatively few types provided plentiful material for the practice of writing constitutional formulæ and the ingenious development of stereochemistry.

The study of the morphology of natural and artificial inorganic crystals during that period seems in comparison to have produced a wealth of useful data, but fewer generalisations. Changes in crystal form due to alteration in chemical composition of closely related substances, above all, those which clearly revealed a marked change in one axial direction, led to premature hypotheses of atomic configuration within the crystal. The concept of molecular volumes leading to the derivation of ' topic parameters ' enabled Tutton, for instance, to derive from accurate goniometric measurements of numerous series of isomorphous salts part of the information which is now obtained from measurements of the unit cell of a crystal structure (28). The changes in topic parameters produced by the substitution of one element by another in two isomorphous salts were, however, interpreted in terms of two assumptions, later to be disproved. Elements were wrongly assumed to increase in atomic size with their weight and the crystal structures of inorganic salts were supposed to contain groups of atoms like molecules.

Morphotropic relationships were discovered in organic compounds and also amongst silicate minerals like the humite series. The accurate work of Fletcher, Lewis, Hutchinson, Miers, Spencer, Herbert Smith and Barker (to name only some of the outstanding English crystallographers of that period) on minerals and inorganic substances prepared a sure foundation for the successes of the X-ray crystallographer. Mention must be made also of the speculations of Pope and Barlow on crystal structure, who, only a few years before the discovery of X-ray diffraction, came very close to the truth. For the first time they regarded a crystal as a geometrical packing of spherical atoms each of a definite size determined by an equilibrium between opposing forces of attraction and repulsion between neighbouring atoms (25). Although their valency-volume theory proved incorrect they described the cubic and hexagonal forms of close-packing (24) and also predicted for simple binary compounds the rock-salt and caesium chloride structures.

A fascinating account of the discovery of X-ray diffraction by a crystal grating in Munich in 1912 and of the first crystal structures to be analysed with the ionisation spectrometer (29) by the Braggs, father and son, is given in Chapter XII of ' The Crystalline State ' (W. H. and W. L. Bragg). W. L. Bragg's idea that X-rays were reflected from the crystal planes provided a simpler explanation of Laue's photographs of blende (ZnS), and by the following year, 1913, the structures of rock-salt, diamond, blende, pyrite (FeS_2), fluorite (CaF_2) and calcite ($CaCO_3$) had been worked out (31). For about ten years the new technique was successfully applied only to simple substances, but was considerably extended in range by the development of the X-ray photography of powders and rotating small crystals. The measurement of the absolute intensities of X-ray diffractions together with the calculated scattering powers of atoms extended analysis to the more complex structures of orthorhombic aragonite (1924) and the sulphates of the barytes group (1925) (30). These were preliminary to the outstanding success of the Manchester school of W. L. Bragg in unravelling the complexities of silicate structures, many of which demanded the evaluation of twenty or thirty parameters (34, 37).

By 1926 the number of research workers engaged on analyses of crystal structures become so numerous that the published work for that year included over 300 separate papers. It was natural that most of the substances first studied should be either those minerals occurring in well-formed crystals or artificially prepared, and comparatively stable inorganic salts. Thus were formulated quite soon after the Braggs' researches the fundamental principles of crystal chemistry, particularly of ionic compounds as distinct from the metals and organic substances. The structure of an ionic crystal is dependent on the geometry of packing as well as on the balancing of the electrical charges of the constituent ions. Each metallic ion tends to surround itself with the largest possible number of anions. No chemical molecule as such appears in the structure, but only groups and radicles as structural units. The effective radii of the constituent atoms and ions govern the shape and dimensions of the co-ordination polyhedra (33). Thus silicate minerals, forming over 90 per cent. by weight of the earth's crust, are now known to be built from SiO_4 tetrahedra (36), and not from series of hypothetical silicic acids. In olivine (37a) the tetrahedra are not linked directly, but are joined together with octahedra of MgO_6 and FeO_6. In the pyroxenes (37b) and amphiboles the tetrahedra SiO_4 are linked into endless chains and bands strung corner to corner and linked sideways by the magnesium and iron octahedra. In beryl (34) six tetrahedra join up to form a ring, and in the micas (37c) endless sheets of tetrahedral groups containing both Si and Al are keyed together by the alkali ions. The properties of clays are largely determined by the same type of sheet structure, although the sheets are less regularly piled and the attractive forces between the sheets are weak. Three dimensional frameworks of linked SiO_4 tetrahedra have been found in the crystal structures of quartz (37), the zeolites and felspars (37d). Although the stereochemistry of all the principal mineral groups are known the more detailed investigations by W. H. Taylor with modern technique of the structure of the microperthite and plagioclase structures and of ' imperfect ' minerals like asbestos are already yielding interesting results. Amongst the principal achievements of the last decade in the field of inorganic structures are the crystal analyses of hydrates like $CuSO_4 . 5H_2O$ (38a) by Beevers and Lipson, of gibbsite by Megaw and of gypsum (38b) by Wooster. English workers have also played a prominent part in the study of thermal and other perturbations of crystal structure. Observations on non-Laue scattering by Preston were extended by Lonsdale particularly to the study of diamonds, some of which, the most perfect, give, in addition to the thermal non-Laue scattering, extra lines and spots not to be readily explained in terms of a new structure or faults.

The early structure-analyses of organic compounds were primarily confirmatory of the molecular arrangements long accepted by the chemist. The X-ray methods can give, however, even in the simplest structures, additional and important information, viz. molecular dimensions and inter-atomic bond-lengths, the shape of the molecule as a whole and the nature of the forces binding the molecules into a crystal structure. W. H. Bragg's measurements of naphthalene and anthracene revealed an increase in the c dimension of 2·5 Å., thus affording the first approximation to the size of the benzene ring, and the crystal structures of both hydrocarbons were completely determined by Robertson in 1933 (32). The crystal structure of graphite (31c) was obtained by Bernal in 1924, who found it to consist of hexagonal sheets of carbon atoms within which the C–C distance of 1·42 Å. is intermediate between distances corresponding to a single and a double bond. The distance of approach between separate sheets held together only by Van der Waals forces is 3·40 Å. This structure explains many of the physical properties of graphite. The first complete X-ray analysis of an aromatic compound was, however, that of hexamethylbenzene by Lonsdale in 1928, who found that the benzene ring has a plane hexagonal form with C–C distance 1·42 Å. and is linked to the CH_3 groups by normal single bonds 1·54 Å. in length (40a). In the structure of solid benzene itself, determined by Cox in 1932, the benzene ring was also found to be a plane hexagon with the dimensions given by Lonsdale. Long-chain paraffins, studied by Müller, were worked out very fully. They contain molecules of a plane zigzag chain of carbon atoms with a C–C distance 1·54 Å. and a tetrahedral inter-bond angle of $109\frac{1}{2}°$. More complex structures soon after elucidated were o-diphenylbenzene by Clews and Lonsdale, 1937; dibenzyl, stilbene, resorcinol, tolane and phthalocyanin (40c) by Robertson and Woodward, 1934–38; cyanuric tri-azide by Knaggs, and methylene-blue iodide by Taylor, 1935.

A variety of less complete but intrinsically important crystal structure investigations have been carried out in recent years which can be reviewed only very briefly here. All of these have given definite stereochemical information where chemical methods alone were not conclusive. The classic work of Astbury (48) on the keratin group of fibrous proteins has been extended to myosin and the study of living muscle in various stages of contraction. The contraction of muscle and the supercontraction of hair involve similar processes believed to be involved in the formation of corpuscular proteins. The latter can be partially unfolded by treatment with urea, thus enabling fibres of industrial importance to be produced from *e.g.* peanut globulin. The investigation of insulin by Crowfoot, of hæmoglobulin by Perutz and Boyes-Watson, and of hydrated lactoglobulin by Riley points to a common basic protein structure (49).

Recently it has been possible to determine the formula and bond-lengths of a compound without assumptions based on organic chemistry and thus to assist materially in the determination of structures. X-ray evidence for flat structures of the pyranose and furanose rings in sugars obtained by Cox and Goodwin has led ultimately to the crystal structure of sucrose by Beevers and Cochran (46). The detailed stereochemistry of cholesteryl iodide has been worked out by Carlisle and Crowfoot and of glucosamine hydrochloride (46) by Cox and Jeffrey; both compounds, like sucrose, contain several asymmetric centres. Bernal and Crowfoot have obtained information on the structures of sterols, vitamins and the sex-hormones, all of which have yielded information of biological importance. Preliminary work on the crystalline viruses by Bernal, Crowfoot and Carlisle shows that good single crystal X-ray photographs can be obtained revealing, like those of hæmoglobin, very large unit cell dimensions (50).

One last example which is outstanding amongst modern structure analyses is the determination of the structure of penicillin (Crowfoot and

Rogers-Low; Bunn and Turner-Jones) (47). Penicillin is an asymmetric molecule of unusual form and its structure yielded only to the systematic attack of three-dimensional Fourier syntheses and Bragg's fly's-eye technique.

For List of Exhibits in this Section see Appendix on page 79.

CHAPTER III

COLLOID SCIENCE AND SURFACE CHEMISTRY

THOMAS GRAHAM, the first President of the Chemical Society, has frequently been designated 'the father of colloid chemistry,' although a number of important contributions had been made by prior workers. Of these particular mention should be made of the unceasing movement of colloidal particles observed in the microscope, termed the Brownian movement in honour of its discoverer, of Way's discovery of base-exchange in soils, and Faraday's studies of the preparation and optical properties of gold sols (51). Faraday showed that these colloidal 'solutions,' although optically clear in the ordinary microscope, actually contained fine particles of dispersed metal, and that the colour change, red to blue, brought about by addition of salts, was due to aggregation (52). He discovered that gelatine could protect gold sols from the coagulating power of salts (53) and suggested that the Purple of Cassius consisted of finely-divided gold associated with tin oxide—a view later confirmed by Zsigmondy.

Graham stands out, not only for his fundamental practical investigations, but also for introducing a classification and nomenclature, much of which is still in current use. (For example, the terms *colloid*, *sol*, *gel*, *peptisation* and *syneresis* were all coined by him.) His principal papers upon colloids, published in 1861 and 1864, were respectively entitled *Liquid diffusion applied to analysis*, and *On the properties of silicic acid and other analogous colloidal substances*. The purification of sols by dialysis (54) is inseparably linked with his name. In addition to pointing out the principal properties which characterise the colloidal state (low diffusivity, absence of crystallinity, and frequently of ordinary chemical reactions) he laid special emphasis upon its biological significance. Graham also studied adsorption phenomena, *e.g.* the removal of iodine by charcoal, which he recognised as a surface phenomenon.

The scattering of light by colloidal suspensions is associated particularly with Tyndall's practical investigations (55, 56) at the Royal Institution, and with Rayleigh's theoretical analysis, while certain further aspects were treated later by Maxwell Garnett. Tyndall's studies of air-borne bacteria in relation to putrefaction were of great topical interest (57).

Of other important investigations carried out towards the close of the last century, two notable theoretical contributions were the independent deduction of the Gibbs adsorption isotherm by J. J. Thomson, and the influence of curvature on the vapour pressure of small drops and the solubility of colloidal particles, by Kelvin. On the practical side, Picton and Linder devised the moving-boundary method for electrophoresis of sols, later developed by Burton, Lewis and others, and also made an extensive study of the properties and coagulation of sols. Lodge's study of diffusion in gels is mentioned in the chapter on Liquids and Solutions (p. 16). Rayleigh contributed a great deal to the theory and practice of surface tension ; for example, he measured the minimum amount of olive oil necessary to lower the surface tension of water and also to stop the movement of camphor particles, an embryonic beginning to the field of surface chemistry, and important at the time, since it enabled the size of such large organic molecules to be estimated.

Ramsden (1903–04) showed how proteins were denatured by adsorption at interfaces ; Pickering (1907 and later) studied emulsification, particularly by solid powders (58), and pointed out the conditions for promoting either the oil-in-water or the water-in-oil types.

Hardy's contributions to the study of colloids, extending over some thirty years from the end of the last century, were both extensive in their range and pioneering in their outlook. Of his early work the quantitative study of the influence of charge and valence of ions upon the coagulation of sols (the Hardy-Schulze rule) is well known (59). His biological interests led him to study phenomena at interfaces, ' surface chemistry ' as it is now generally termed. The concept of differences in the force-field around long-chain hydrocarbon derivatives and its bearing upon spreading and molecular orientation at surfaces was also developed by him. His practical contributions included work on friction and lubrication (60), an aspect later developed by Bowden and his co-workers, and the effect of films upon the stability of bubbles blown beneath a surface (61).

Surface chemistry owes much to the later work of Adam, and to Rideal and his school at Cambridge. The former put the study of insoluble monolayers by the ' film balance ' (62) upon a sound experimental basis ; Rideal's school developed the study of monolayers by surface potentials and studied in particular surface reactions upon both aqueous and solid surfaces (63) (p. 23). The work of Roberts upon adsorption at really clean metal surfaces was outstanding.

Amongst other early investigations of the present century those of Donnan and of McBain are notable. The former carried out the first experimental test of Gibbs adsorption isotherm (64) ; he also studied membrane equilibria and the relation between surface tension and emulsification. Adair later developed the study of membrane equilibria (65) and also molecular weight determination of proteins by osmotic pressure (66).

McBain suggested that the combination of low osmotic activity (67) with high electrical conductivity of soap solutions could be accounted for by the existence of ionic micelles, aggregates of many ions : Hartley later elucidated their structure and put the theory of dilute soap solutions on a sound basis. Further contributions were made by Bury, Lawrence and others.

Of other contemporary workers in colloid science Hatschek examined such topics as the kinetics of coagulation, the viscosity of emulsions, and the reduction of gold salts in gels (68) ; Whytlaw-Gray and his co-workers put the practical study of smokes upon a sound foundation.

A number of more recent theoretical advances should be mentioned, such as the work of Taylor on the viscosity of emulsions and the break-up of drops in definable fields of flow, and that of Jeffries on the viscosity of systems containing asymmetric particles.

In the field of polymers Astbury's pioneer X-ray studies have thrown much light on the structure of protein fibres, as well as on contraction phenomena in wool and muscle proteins. Melville is noted for his work on the kinetics of polymerisation reactions, Gee for his substantial contributions to the thermodynamics of rubber solutions. In the difficult field of rheology Scott Blair has carried out very valuable exploratory studies.

EXHIBITS

Colloid Science and Surface Chemistry

51. Examples of Faraday's gold films, sols and gels.
    (Lent by Science Museum and Royal Institution.)
52. Effect of salts on gold sols (after Faraday).
53. The protective action of gelatine upon gold sols (after Faraday).
54. (*a*) Graham's dialysis bowl. (*b*) Simple dialysis apparatus.
    (Lent by the Science Museum.)
55. Demonstration to illustrate the lateral scattering of light by colloidal suspensions (Tyndall beam).
56. Tyndall's ' Blue Sky ' tube (de la Rue's replica).
    (Lent by the Royal Institution.)
57. Tyndall's ' Germ Box ' and broth solutions.
    (Lent by the Royal Institution.)
58. Emulsification by solid powders (after Pickering).

59. Illustrating the Hardy-Schulze rule for the effect of charge and valence on coagulation of sols by salts.
60. (*a*) Reconstruction of apparatus used by Hardy in his studies of friction and lubrication. Also an outline of his main conclusions. (*b*) Modifications of Hardy's views based on more recent work.
61. Effect of surface films upon the stability of bubbles (after Hardy).
62. Film balance for the study of insoluble monolayers upon aqueous solutions (Adam).
63. Techniques for the study of films upon liquid and solid surfaces (Rideal and Cambridge school).
64. Reconstruction of the apparatus used by Donnan to test the Gibbs' adsorption isotherm.
65. Experiments to illustrate membrane equilibria (Adair).
66. Osmometers for protein solutions (Adair).
67. (*a*) Dew-point lowering by potassium fatty acid salts (McBain).
    (*b*) Illustrating the solvent properties of soap micelles for an oil-soluble dye (Hartley).
    (*c*) An experiment to illustrate micelle formation in aqueous soap solutions (Hartley).
68. Reduction of gold salts in gels (Hatschek).
    (Lent by the Science Museum).

Exhibits Nos. 52, 53, 55 and 58–67 were prepared and arranged by Dr. A. E. Alexander.

CHAPTER IV

LIQUIDS AND SOLUTIONS

General properties of liquids and solutions

INTEREST in the physical properties of liquids and solutions, and their relation to chemical structure, grew very rapidly during the second half of the nineteenth century, side by side with the great advances in organic chemistry. Much of the development was due to the British chemists who refined the experimental methods and accumulated reliable data. Refractivity and its relation to structure was studied by Gladstone and Dale (1858–70); the Kerr effect was described in 1875. Magnetic rotatory power was discovered by Faraday in 1846, and its relation to structure was studied in a long series of papers in the *Journal of the Chemical Society* by H. W. Perkin (1884–1907).

The systematic study of the absorption of light by solutions dates from the pioneering work of W. N. Hartley (1879) in the visible and ultra-violet regions (p. 58), and its extension into the infra-red by Abney. The value of a comparative study of absorption spectra in elucidating the structure of organic compounds was first demonstrated (*e.g.* for isatin) by Hartley and Dobbie, and the development of this field of research is especially associated with the names of Baly, Desch, Stewart, Hewitt and other British chemists.

The work of Thorpe and Rodger on the viscosity of liquids is classical, and the viscosities of mixtures were studied by A. E. Dunstan. The work of Ramsay and Shields on molecular surface energy (1893) is well known, as is that of Sugden. Sugden made improvements in the measurement of surface tension, used Macleod's equation to introduce the *Parachor* (1924) (70), and showed the value of this property in the general revision of formulæ which followed on the adoption of the electronic theory of valency.

Turning to the more general theory of solutions, Henry's Law and Blagden's Law recall two early workers. In the period under review the outstanding contributions are the very well-known osmotic pressure measurements of Berkeley and E. G. J. Hartley, and the pioneer work of Graham on diffusion (1850) (71) which laid the foundation of the science of colloids. The techniques devised by Ramsay and Young for the measurements of vapour-pressures and boiling-points should also be mentioned, and the use by Ramsay of the vapour-pressure-depression method to find the molecular weights of the metallic elements (1889). The development of distillation practice is referred to elsewhere (p. 3), but a note should be made here of the fundamental work on this subject of Sidney Young.

In recent times, Guggenheim and Butler have done important work on the thermodynamics of solutions, and the paper of Bernal and Fowler on the structure of water (1933) should be noted as a contribution to modern theories of liquid structure.

Theoretical electrochemistry

The foundations of the theory of electrochemistry were laid more than a century ago by Faraday when he discovered the laws of electrolysis known by his name, introduced the nomenclature still in use, and showed how to measure the quantity of electricity passing through a circuit by means of his electrolytic voltameter (72). He was followed by Daniell, who studied the changes in concentration which he found to occur around the electrodes during electrolysis, and proved that the current was carried by ions of *solute.*

Lodge (1886) showed how the velocity of ionic migration could be observed and directly measured, and the modern ‘ moving boundary ’ methods have evolved from this through the work of Whetham (1893), Masson and Denison and Steele (1901–06). G. S. Hartley's ‘ balanced boundary ’ apparatus illustrates this elegant method in its most modern form (73).

Many consequences of the electrolytic dissociation theory of Arrhenius have been described in the *Journal of the Chemical Society*. Methods of measuring the hydrolysis of salts were put forward by J. Walker (reaction-velocity method), Farmer (distribution method), and Tizard (indicator method); and Walker studied the dissociation of very weak acids (1900), and elucidated the equilibria in solutions of amino-acids (1904). More recently, Lowry (1923), simultaneously with Brönsted, outlined the modern view of acid-base equilibria.

The Debye-Hückel theory was foreshadowed in the papers of Sutherland (1902) and Milner (1912), and Sand (1923) predicted the high frequency and high voltage effects. On the experimental side, notable advances in conductivity technique at high dilutions were made at Oxford. The Hartley and Barrett cell (1913) has the advantages that the conductivity of the solvent may be determined *in situ*, that contamination from carbon dioxide and dust particles is prevented, and that adsorption errors are minimised (74). Great attention was also paid to solvent purification, and it was largely the precise measurements of H. Hartley and his collaborators (1925–31) in methyl and ethyl alcohols and other solvents that established the general applicability of the Debye-Onsager theories. Coates, Philip and Martin have also contributed accurate data for non-aqueous solutions.

The voltaic cells of Daniell (Cu, $CuSO_4$, $ZnSO_4$, Zn) (75), Grove (Zn, H_2SO_4, HNO_3, Pt) and Smee (Zn, H_2SO_4, platinised silver) deserve mention. Sand, in addition to a fundamental study of concentration polarisation, made many improvements in electrochemical methods of analysis.

The problem of overvoltage has engaged the attention of many British chemists. Newbery first used a commuting device for studying intermittently polarised electrodes, and this method has been developed by Glasstone, and later by Hickling, whose measurements at intervals as small as 10^{-5} seconds after interruption of the polarising current have given new important results. Butler has also studied the discharge of hydrogen and oxygen at metal electrodes, and Bowden and Rideal's precise measurements at very low current densities have led to interesting results.

ELECTRODEPOSITION

Electrodeposition comprises three principal branches of technology:—

1. *Electroplating*, which usually concerns the production of thin metallic coatings for decoration and protection of the basis metal, but also includes the production of thick deposits, usually of nickel or chromium for engineering purposes, *e.g.* to salve worn or overmachined components. Allied processes such as the anodic oxidation of aluminium, anodic polishing and rubber deposition may be conveniently included in this branch.

2. *Galvanoplasty*, comprising electroforming and electrotyping in which processes electrodeposits are built up on moulds or forms and then detached to provide a replica of the original form.

3. *Electro-winning and electro-refining*, in which electrodeposition is used to extract metals from their ores or to refine impure metals.

British electrochemists have made important and indeed basic contributions in all these fields throughout the past century. Though preceding the period under review by a few years no account of British progress in electrodeposition, however brief, should omit reference to Faraday's fundamental work on electrolysis and on electromagnetic induction upon which all subsequent progress ultimately depended.

In the field of electroplating the first few years of the period were marked by very rapid development. Thus industrial electroplating commenced with the patent of Elkington and Wright (1840) for depositing silver from double cyanide solutions, which process has remained substantially unaltered to the present day. In 1843, Alfred Smee, Surgeon to the Bank of England, in the second edition of his book, *Elements of Electrometallurgy*, described solutions for the deposition of some seventeen elements including all the metals which are commonly electroplated to-day with the exception of chromium (76, 78). The development of industrial electroplating, at first confined to copper, silver and gold, was retarded for some thirty years mainly by the lack of adequate electric power, but the introduction of the Wilde dynamo (1866), the Bessemer steel process (1855), and the development of the first successful nickel-plating solution in the U.S.A. (Adams, 1869) led to a rapid expansion during the last quarter of the nineteenth century. Nickel, brass, zinc, and later tin, lead and cadmium (*c.* 1920) were added to the list of commercially deposited metals. The commercial application of chromium-plating around 1925 was primarily an American achievement (Sargent, 1920), though the process had been envisaged much earlier (Junot, 1853 ; Bunsen, 1854).

The important process of applying thick electrodeposits for the salvaging of mechanism components was first introduced by the British Army in France during the 1914–18 war and has subsequently developed extensively both for Service purposes and industry at large. Problems concerning the mechanical properties and adhesion of electrodeposits arising from this new application of electrodeposition have been largely solved by research workers in British Government laboratories.

Another British achievement was the discovery by Bengough and Stuart, in 1924, of the anodic oxidation process, now very widely practised, for the protection and decoration of aluminium and its alloys.

In the field of galvanoplasty pioneer work was done by Jordan, Spencer and Murray in the first years of the century under review. The importance of the resultant development of electrotyping in the printing trade cannot be over-emphasised. The Elmore process (1891) enabled tubes and sheets to be produced by deposition upon a rotating mandril, whilst the work of Cowper Coles and others led to further developments, for example, to reproducing parabolic mirrors by deposition on a master glass mould.

Electro-refining and electro-winning of metals were commenced in this country with Elkington's copper-refining plant in South Wales (1869), whilst Brunner Mond and Company commenced electro-refining of zinc in 1897.

During the past twenty-five years scientific research in electrodeposition has been very active, especially in the U.K., the U.S.A. and Germany. British scientists have made an important contribution to the sum total of knowledge so gained, much of which is recorded in the *Journal of the Electro-depositor's Technical Society* (founded 1925). Among the subjects investigated are the following : Bright plating, anodic polishing, rhodium, platinum and palladium plating, alloy deposition, plating on plastics, structure and properties of electrodeposited metals, physical testing of electrodeposits, etc., etc.

CORROSION AND PASSIVITY

The term ' Corrosion Reaction ' is generally held to cover any change in which a metal passes from the elementary to the combined condition. Such changes obey well-defined laws, capable of reasonable interpretation and therefore possessing scientific interest, although often neglected in chemical text-books. The attention paid to the subject arises largely from the damage caused in industry by corrosion reactions ; Dr. J. C. Hudson has calculated that the cost of protecting ferrous metals in the United Kingdom alone may reach about £40,000,000 per annum.

' Passivity ' is the name given to a peculiar state sometimes assumed by a metal in which it remains unaffected by a reagent which would normally attack it. The phenomenon is generally attributed to an invisible film. Actually most metals on exposure to dry air quickly develop an invisible film, but often it is too cracked to be completely protective. Direct combination between a metal and a non-metal (*e.g.* dissolved oxygen) frequently leads to film-formation, which slows down further attack. Electrochemical reactions more often produce soluble products instead of protective films ; consequently the mechanism of some of the more destructive corrosion-processes is an electrochemical one.

Although the first suggestion of the electrochemical character of corrosion came from France, the essential inter-connection of chemical and electrical changes was established by the researches of Michael Faraday—especially those published between 1834 and 1840. An interesting correspondence between Faraday and his Swiss friend, Professor Schönbein, published in 1836, first brought the phenomenon of passivity to general notice.

After Faraday's time, the development of the electrochemical aspect of corrosion was mainly conducted abroad—rather especially in Sweden. Interest in corrosion continued, however, among British chemists, and in the early years of the present century, there was much discussion at the Chemical Society's gatherings as to whether oxygen, carbonic acid, hydrogen peroxide or some other substance played the predominant role in corrosion. Among those prominent in these discussions may be mentioned Dunstan, Moody, Tilden, Friend and Lambert; the experimental technique of the latter deserves special mention.

During the war of 1914–18, corrosion became a problem of national importance, owing to the fact that warships were being kept in port as a result of condenser trouble. The work of the late Dr. Bengough and his colleagues, particularly May, dealt with the difficulties so successfully that, at the outbreak of the Second World War, condenser corrosion had ceased to be a major problem. Another practical result of Bengough's work has been the well-known anodising process for aluminium alloys. Later, Bengough carried out distinguished work on the scientific aspect of corrosion by salt solutions, largely based on an apparatus in which the progress of corrosion was measured by the observation of oxygen consumed in the reaction. His colleague, Dr. Vernon, has conducted numerous investigations which to-day form the basis of our knowledge of atmospheric corrosion. Amongst the achievements of this research group may be mentioned (1) a study of the green patina formed on copper roofs, (2) the part played by dust particles in the rusting of iron, and more recently (3) the development of a high-speed rotor apparatus for simulating, in the laboratory, the passage of painted ship's plates through the sea. Extensive studies of atmospheric corrosion have also been carried out by Dr. J. C. Hudson, who first worked on non-ferrous and then on ferrous materials.

The interesting researches of Dr. E. S. Hedges, published in the *Journal of the Chemical Society* about 1925–31, were particularly concerned with periodic alternations between the passive and the active state. The investigations at Cambridge University, carried out by the research group associated with U. R. Evans, have included (1) the measurement of micro-currents flowing over a corroding surface, which are found to be sufficiently strong to explain the corrosion, and (2) the study of thin films on metals (80).

EXHIBITS

Liquids and Solutions

70. *The Parachor.* Illustrated by *Journal of C.S.*, 1924, pp. 1177–1179.
71. Graham's osmometer liquid diffusion cells.
    (Lent by the Science Museum.)
72. Faraday's electrolysis apparatus and standard cell.
    (Lent by the Royal Institution.)

73. Velocity of ionic migration (Lodge, Masson, Hackley).

74. Hartley and Barrett cell.

75. An early Daniell cell.

76. Electrotypes by Smee and Warren de la Rue.
(Lent by Mr. G. H. Gabb.)

78. Very early electrotypes, electroformed plaques and earthenware crock, used by Elkingtons.
(Lent by University College, Swansea.)

80. Corrosion. Exhibit to illustrate work on metallic corrosion.
(Prepared by Dr. U. R. Evans and the Chemical Research Laboratory.)

CHAPTER V

CHEMICAL REACTIONS

1. RATE OF CHEMICAL CHANGE

(*a*) *Homogeneous reactions*

SIXTEEN years after Wilhelmy's experiments on the rate of inversion of cane sugar, Harcourt and Esson (1865–66) made a careful study of the influence of concentration and temperature on the velocity of several reactions in solution. In the course of this work they

(*a*) made the first detailed quantitative kinetic study of a bimolecular reaction,

(*b*) made the first detailed mathematical analysis of kinetic data, including the complications arising from reactions,

(*c*) established the incidence of autocatalysis and periods of induction in chemical reactions.

In 1890 O'Sullivan and Tompson, in a thorough study of the inversion of cane sugar by invertase, showed that the course of an enzyme-catalysed reaction is kinetically indistinguishable from that of any other catalytic reaction. In 1904 Lapworth, by his measurement and interpretation of the kinetics of the halogenation of ketones, provided the first demonstration of how kinetic data could throw light on the mechanism of an organic reaction and initiated a new 'kinetic' era in theoretical organic chemistry.

Dixon (1884 onwards) made some of the earliest observations on homogeneous catalysis in gas reactions, such as the influence of moisture on the explosibility of carbon monoxide-oxygen mixtures and of nitrogen peroxide on hydrogen-oxygen mixtures. He was also responsible for the accurate and systematic measurement of flame velocities in gaseous mixtures. Baker (1885–1929) investigated the puzzling effects of intensive drying on chemical reactivity and various physical properties of substances. Bone (1902 onwards) made exhaustive studies of the mechanism of the combustion of hydrocarbons and of combustion at high pressures (p. 27).

In 1898 Slater Price, by showing the enhanced catalytic effect of iron and copper ions on the persulphate-iodide reaction when present simultaneously, established one of the earliest recorded instances of promoter action. Sir James Walker (1895–1903) investigated the rate of transformation of ammonium cyanate into urea. He elucidated the complications arising from the reversibility of the reaction and also made some of the earliest observations on the influence of the solvent on reaction velocity. Orton (1909 onwards), like Lapworth, made fruitful application of kinetic studies to the elucidation of the mechanism of organic reactions by his studies of the halogenation of anilides. Dawson (1915 onwards), by his painstaking dissection of the complexities arising from the simultaneous catalytic effect of a variety of molecular species, helped to lay the foundations of the general theory of acid-base catalysis. W. C. McC. Lewis (1915–22), in the course of ultimately fruitless efforts to establish the ‘ radiation ’ theory of thermal reactions, made calculations of the molecular statistics of a bimolecular gas reaction and thereby one of the earliest approaches to an *a priori* calculation of the velocity of a chemical reaction. Lowry (1923 onwards), by his enunciation (simultaneously with and independently of Brönsted) of the modern definition of acids and bases greatly contributed to our understanding of acid-base catalysis as also by his experimental investigation of a number of protolytic reactions. Hartridge and Roughton (1923) showed how the speed of an extremely rapid reaction could be studied by the measurement of an appropriate physical property of the reactant mixture at various points along a tube through which it flowed rapidly (81).

Hinshelwood (1922 onwards) carried out extensive measurements on the kinetics of homogeneous gas-reactions. In the course of this work he established the broad validity of the collision-theory of reaction-velocity. In the field of reactions in solution he showed how the influence of structure, solvent and other factors in reactivity could be analysed and interpreted in terms of activation-energy factors and probability factors. Lindemann (1922) showed how a reaction could be kinetically of the first order and yet derive its activation energy from collisions. Polanyi (1922 onwards), by his investigations of the kinetics of reactions involving atoms, threw much light on a category of reactions of great theoretical importance. He collaborated with Eyring in formulating the ‘ activated complex ’ theory of reaction velocity which by its shift of emphasis has proved a useful complement to the collisional approach to kinetic problems. Polanyi has also done valuable pioneer work in the correlation of bond strengths with chemical reactivity. Melville (1931 onwards) has studied the kinetics of the thermal reactions consequent upon an initial photochemical process. More recently he has thrown much light on the nature of polymerisation processes by a study of their kinetics in the gas phase and in solution.

(*b*) *Heterogeneous reactions and surface action*

Some of the earliest recorded instances of surface catalysis are to be found in the observations of Davy (1817) and Faraday (1833) on the catalytic activity of platinum (90). In 1868 Deacon discovered the process of chlorine-manufacture bearing his name. This classic example of catalysis was one of the earliest instances where a catalyst was deliberately chosen rather than accidentally stumbled upon. Bone (1905–26) played a leading part in the scientific investigation and practical application of 'surface combustion,' a catalytic process of great practical importance.

The work of Strutt (1912) on the reaction between ozone and silver oxide provided one of the earliest and, at the same time, one of the most clear-cut applications of molecular statistics to the speed of a reaction. Palmer and Constable (1920–27) made one of the most systematic studies of a heterogeneous reaction in their work on the dehydrogenation of alcohols at a copper surface. These experiments threw a good deal of light on the distribution of active centres in a catalyst and on the nature of the adsorption process. H. S. Taylor (1920 onwards), an Englishman by birth though working in America, has played a very active part in the development of ideas on heterogenous catalysis. His name is especially associated with the view that the surface of most catalysts is far from homogeneous in activity and with the establishment of the distinction between 'activated' and 'Van der Waals' adsorption. Hinshelwood (1924 onwards) showed how the kinetics of a number of heterogeneous gas reactions could be interpreted in terms of Langmuir's picture of gaseous adsorption and also clarified our ideas about the energy of activation in surface reactions. A number of British chemists, notably Armstrong, Hilditch and Maxted, have concerned themselves for many years in the problems of heterogeneous catalysis and its industrial applications and have added considerably to our knowledge of catalyst poisoning and promoter action.

Since 1920 Rideal has worked extensively on a wide variety of problems in surface chemistry, including the study of adsorption from gases and solutions, heterogeneous catalysis and the properties of monolayers, and in the latter connection more particularly the investigations of surface potentials and of reactions taking place in monolayers. Garner (1924 onwards) has made extensive measurements of the heat of adsorption of gases (92). His observation of the considerable heats of adsorption of the first portion of oxygen on charcoal played an important part in establishing the notion of active centres.

The name of Adam is permanently associated with the study of monolayers, upon which he has carried out a wide range and variety of experiments since 1922. Quastel (1926–36) has carried out important pioneering researches on reactions catalysed by enzymes and bacteria. Roberts (1930 onwards) has made a number of careful studies of the adsorption of gases on wires which have considerably extended our knowledge of the adsorption process from the physical point of view. In the same connection should be mentioned the theoretical researches of Lennard-Jones into the physical process of adsorption. Allmand (1930 onwards) has made a number of measurements on the adsorption of gases on solids and the associated heat changes. He revealed the existence of apparent discontinuities in certain adsorption isotherms, a puzzling phenomenon that is still very imperfectly understood.

II. CHAIN REACTIONS

In the development of the theory of chain reactions several of the modern English schools have taken a prominent part and among them may be mentioned Oxford, Cambridge, London and Manchester (Allmand, Egerton, Garner, Hey, Hinshelwood, Melville, Norrish, Polanyi, Rideal, Waters and others). It may be noted also that F. O. Rice, who has contributed much to the theory of chain reactions in the decomposition of organic compounds, although working in America, is an Englishman by birth. The principal sections of this field in which British chemists have made contributions are : experimental demonstration of chains in thermal reactions such as the hydrogen-oxygen combination ; investigation of the varied and complex properties of chain systems (hydrogen-oxygen, hydrogen-chlorine, and so on) (87, 94) ; demonstration of free radical chains in the decomposition of organic compounds ; exploration of the possibility of chains in solution and in solid reactions ; relation of chains to explosions, anti-knock action, etc. ; highly dilute flames of alkali metals and halogen compounds (86). A whole separate branch of the subject has been developed in the study of the polymerisation reactions. In this, various academic schools have been concerned and the industrial contribution has been outstanding not only to technical, but to pure chemistry (I.C.I. Alkali Division and others).

III. REACTION MECHANISM

Our understanding of the mechanism of chemical reactions was at first based on an intuitive interpretation of available chemical knowledge, and has gradually grown in certainty through designed experiments and the application of every kind of physical technique. British chemists have been prominent in both phases, and have often provided the basic ideas which have been developed in detail elsewhere.

Lapworth was among the first to provide a reasoned advocacy of the importance of ionisation in organic reactions, and his studies of cyanhydrin formation and the halogenation of acetone are the classical instances of the use of kinetic measurements to elucidate reaction mechanisms. Lapworth's work covered a wide range of organic reactions, and particular classes of reaction were later studied more intensively by other chemists ; for example, prototropic reactions (catalysed by acids and bases) by Lowry, Dawson and Bell, and migration reactions by Orton. The more general aspects of reaction mechanism have been greatly advanced since the time of Lapworth by Robinson and Ingold. Robinson has based his conclusions largely on a wide review of organic reactions, while Ingold has made an intensive study of a smaller number of reactions, using physico-chemical methods such as isotope exchange, optical activity and detailed kinetic analysis. The topics treated by Robinson and Ingold include benzene-substitution, migration reactions, esterification and hydrolysis, and the effect of substituent groups upon reactivity. Other recent workers in this field include Hughes, Bennett, J. W. Baker and Watson.

While Robinson and Ingold have envisaged chiefly ionic reaction mechanisms, Waters and Hey have shown that many organic reactions involve the production of free radicals or atoms in the liquid phase. The production of free radicals or atoms in the gas phase often leads to a complex chain of reactions, and this aspect of reaction mechanism has been dealt with by Hinshelwood for explosion reactions, Rideal for surface reactions and Melville for polymerisations (88, 89), while photochemical investigations by Bowen and Norrish have thrown much light on the part played by atoms and radicals in thermal reactions.

The work mentioned above is chiefly concerned with the qualitative nature of reaction-mechanisms, and it is only recently that we have obtained some insight into the nature and magnitude of the forces involved in the act of reaction. This field has been explored particularly by Polanyi and Evans, partly by experimental work on the reactions of sodium vapour with halides, and partly by theoretical investigation (82, 84-6). The same problem has been tackled from a different point of view by Hinshelwood in his kinetic studies of substituent and solvent effects in certain organic reactions.

IV. PHOTOCHEMISTRY

Photography

Wedgwood and Davy (1802) produced images on paper treated with silver nitrate and exposed under the 'solar microscope.' Talbot (see *Pencil of Nature*, 1844) in 1835 produced the first photograph of modern type on paper

(Lacock Abbey) using a camera. He used concentrated sodium chloride solution as a fixer. Later (1841) he was enabled to use much shorter exposures by *developing the latent image* with gallic acid. Sir Wm. Herschel discovered the method of *fixing* with hypo. F. Scott Archer (1848) used collodion for photographic *film*, and Maddox later prepared dry *gelatine* films containing silver bromide. Bennett discovered how to increase the sensitivity of films by heating (95).

Abney (1882) investigated the sensitivity of photographic plates, while F. Hurter and V. C. Driffield (1890) discovered the relation between photographic blackening and light intensity and exposure, embodied in their 'speed number.' Sheppard (1927) discovered 'sensitising specks' on photographic silver bromide grains produced by the action of impurities (thiocarbamides) in the gelatine. This enabled the production of plates of high and uniform sensitivity to be carried out under scientific control. The technical side of photographic film production was developed under Dr. C. E. K. Mees, F.R.S., Vice-President in charge of Research and Development, Eastman Kodak Co. We may further note the synthesis of infra-red sensitising dyes (96) by Mills and Hamer (1920–30), while Mott and Gurney (1938) have contributed much to the physical theory of the action of light and of development in terms of *electronic* and *ionic* movements.

Other fields of photochemistry

J. W. Draper (1841) enunciated the law that only light actually absorbed can produce photochemical action, and Sir Henry E. Roscoe (1857) worked on the photochemical combination of hydrogen and chlorine, a subject which received further attention from D. L. Chapman and from Allmand.

In recent years there has been a much-increased interest in photochemistry. The principal subjects of study have been photochemical kinetics, and the photochemistry of organic compounds (93). Style, Goodeve, G. S. Hartley, Pearson, Bowen, Thompson and Griffith are among the chief workers in this field. Rideal has studied the photochemistry of surfaces ; Norrish, that of carbonyl compounds ; and Melville, photochemical polymerisations. The subject of photosynthesis has received considerable study from Baly and his school, while Mitchell has developed the interesting subject of asymmetric photosynthesis.

V. FLAMES AND GASEOUS EXPLOSIONS

Davy (1815–19) laid the foundation of most subsequent investigations upon the subject. He established that ignition of an explosive mixture depends upon the temperature of the surroundings (ignition temperatures) ; that flame propagation is determined by mixture composition (limits of inflammability) ; that there is a limiting reduced pressure for flame propagation ; that there is also limiting tube diameter—this led to the Davy safety lamp (100). He estimated flame-temperatures and discovered both slow and incandescent catalytic combustion. He described flame as ' aeriform ' or gaseous matter heated to such a degree as to be luminous. Faraday (1834–35) studied catalytic combustion. His lectures on *The Chemical History of a Candle* (1848–49, 1860–61) are classical.

H. B. Dixon established a famous school of combustion at Manchester (1886 onwards) ; he developed recording cameras for the study of flame travel, with particular reference to the initiation of detonation ; he measured detonation velocities and modified Berthelot's equation covering their theoretical interpretation. With Coward (1909) he developed the concentric tube method, and with Crofts (1910) the adiabatic compression method for the determination of ignition-temperatures ; subsequently the concentric tube method was adapted for work under pressure (1924) (97). He discovered the ' promoter action of nitrogen peroxide.' D. L. Chapman (1899) developed the modern theory of the explosion wave (detonation).

Smithells and Ingle (1892) devised the flame separator revealing the nature of the inner cone of a Bunsen flame (99). They established the composition of the interconal gases, and Smithells and Dent (1894) studied the combustion of cyanogen. V. B. Lewis (1892) propounded an ' acetylene ' theory of the luminosity of hydrocarbon flames. Bone (1902–12) developed the hydroxylation theory by means of both ' slow ' and ' explosive ' combustion of hydrocarbons. With McCourt (1909) he established flameless incandescent surface combustion.

The infra-red emission from flames was measured by Callendar (1910), Hopkinson and David (1910), W. E. Garner (1926 onwards), and H. Hartley (1929). R. V. Wheeler and collaborators (1912 onwards) measured the speeds of ' uniform ' flame propagation through many gaseous explosive mixtures. A. G. White (1919 onwards) studied extensively limits of inflammability.

The electrical ignition of explosive mixtures was studied by W. M. Thornton (1914), Morgan (1919), Wheeler (1920), and more particularly by G. I. Finch (1926 onwards). Tizard and Pye (1922) studied the spontaneous ignition of hydrocarbon-air media by the adiabatic compression method, with particular relation to the problems of the internal combustion engine. They also determined the part played by dissociation in relation to pressure development in gaseous explosions.

Bone, Newitt and Townend (1921 onwards) carried out a series of investigations on gaseous explosions at high pressures, establishing an abnormal yield of oxides of nitrogen with carbon monoxide ; extensive data on calculated flame-temperatures, heat-capacities and flame-spectra also accrued. Bone and Fraser (1927 onwards) examined further the phenomena concerned with detonation by means of the Fraser high-speed camera (98). Payman (1930) also covered a parallel field by means of both direct and indirect (Schlieren) photography. The results established the importance of compression and shock waves in such explosions.

Egerton (1926 onwards) studied hydrocarbon combustion with particular reference to behaviour in the internal combustion engine. He established the formation of peroxidic bodies with a special sampling device and indicated by parallel laboratory experiments their likely influence on the problem of 'knock.' He propounded a theory of anti-knock action. Townend (1933 onwards) established the two-stage mechanism of the spontaneous ignition of the higher hydrocarbons, etc., a 'cool' flame being the precursor of a second stage initiated by peroxide breakdown; this mechanism is probably that responsible for engine 'knock.' This work was extended (1938 onwards) to the 'normal' and 'cool' flame systems in cold media using artificial ignition. In a separate field, he (1939 onwards) established flame speed (ignition velocity) as a physical constant independent of environmental factors, and demonstrated flame-stability on a burner-port in relation to ignition velocity and the flow state.

David (1928 onwards) demonstrated latent energy in flame gases, attributed by Gaydon (1940) to a metastable CO_2 molecule. Gaydon also studied extensively flame spectra and identified oxygen atoms by their reaction with NO. Dooley and Whittingham (1945) also identified oxygen atoms by the formation of sulphur trioxide mists, and Smith (1942) identified the recombination of hydrogen atoms as responsible for the chemiluminescent effects observed on promoted surfaces in contact with flames.

VI. EXPLOSIVES

Within the period of this review a scientific study of explosives was made by Sir A. Noble, in his *Researches on Gunpowder*, on the determination of pressure developed and products formed when gunpowder was fired, 1871–1906; and by Abel, from 1880 to 1894, in his extensive researches on guncotton (discovered by Schönbein in 1845–46), including the chemistry of guncotton, the method of manufacturing it, its safe storage, and a method of detonating it when wet. The primary detonating agent, mercury fulminate, had been described by Howard in 1800.

Nitroglycerine, discovered by Sobrero in 1846, was first manufactured by Nobel abroad, but its early manufacture and his mixture of nitroglycerine with soluble nitrocellulose, blasting gelatine, were improved by the Ardeer chemists before 1890.

Later improvements in the manufacture of these substances are the displacement process for nitroglycerine and for nitrocellulose, and the method of stabilising the latter (Robertson).

Propellants

A colloidal propellant was made by Nobel by incorporating nitroglycerine with soluble nitrocellulose, while the British propellant, cordite, was made with nitroglycerine using acetone as solvent. Sporting-powders of fibrous or partially gelatinous nitrocellulose were evolved in this country.

The stability of cordite was investigated by Robertson, who determined the temperature coefficient of decomposition of nitroglycerine, of guncotton and of cordite. It was proved that the life of cordite was a function of temperature of storage and that the third ingredient, mineral jelly, restrained the decomposition of the esters. A method of determining the residual life of cordite emerged, the silver vessel test.

The calorimetry of propellants was studied experimentally by Noble, Robertson, Macnab and Leighton, and many important data obtained on heat values and on the metamorphosis of the explosives to gases.

High explosives

For tetryl, the intermediate between the detonator and the main explosive for shells and bombs, a manufacturing process was evolved by Silberrad and Merriman, while Farmer determined its stability by a method which has proved of great use for many other explosives.

For trinitrotoluene, which was not made to any extent in this country before 1914, a cyclic process of nitration was worked out at the Research Department, Woolwich, as was also the high explosive amatol (ammonium nitrate and trinitrotoluene). Besides proving their stability in warm environment, that Department also conducted many investigations on the chemical and physical properties of these explosives, including such matters as viscosity of nitrocellulose (Gibson, Masson), isomerides of nitrocellulose (Brady), heat of formation (Garner and Abernethy), determination of sensitiveness (Rotter), measurement of pressure developed on detonation by Hopkinson bar (Quinney), while Robertson and Garner (101) solved the question of determining the calorific value of explosives detonated in their own volume in a calorimetric bomb.

Commercial explosives

Great advances in this country have been made in the use of commercial explosives for fiery mines and much valuable research conducted for the purpose of combating gas- and dust-explosions in mines.

Explosives before and during the War of 1939–45

Previous to the last war a method for the manufacture of cyclonite was worked out by the Research Department, Woolwich, so that its supply was ensured. This explosive has much higher energy than trinitrotoluene and is stable and safe to handle. The same Department brought also a stable solventless and also a flameless propellant.

During the war explosives received an intensive study both departmentally and by a large number of committees set up by the Ministry of Supply.

Only a portion of this great volume of work has been so far published, but it may be claimed that knowledge has been advanced in such subjects as the theory of the initiation of explosives, the kinetics of decomposition of explosives, the nature and progress of the detonation wave, the phenomena of detonation including its measurement, the theory of sensitiveness of explosives to impact and friction, the cause of concentration of energy in the Munroe effect, flamelessness in guns, the most effective fillings for large bombs, incendiary compositions and the design of many new components in which explosives were used. Many important new techniques have been evolved, such as that for measuring pressures set up by detonation in air at a distance from the source, a photographic recording of the earliest stages of detonation and an X-ray cinematographic recording of explosive effects.

EXHIBITS

Chemical Reactions

81. Hartridge Roughton reaction tube. Used in the study of the speed of an extremely rapid reaction.
    (Lent by Professor H. Hartridge.)
82. Potential energy surface. Models.
    (Lent by Professor M. G. Evans.)
83. Phase rule diagrams. Model illustrating typical phase rule diagram.
    (Prepared by Imperial Chemical Industries Ltd.)
84. Model illustrating substitution reactions, showing retention or inversion of optical configuration.
    (Lent by Professor M. Polanyi.)
85. Model illustrating steric hindrance and also illustrating incidence of the activation energy in chemical reactions.
    (Lent by Professor M. Polanyi.)
86. Sodium-halogen dilute flame lamp set up in way normally used, together with drawing illustrating functions of the various parts.
    (Lent by Professor M. Polanyi.)
87. Chain reactions. Apparatus used in study of chain reactions and chemical kinetics.
    (Lent by Professor Norrish.)
88. Polythene. Exhibit designed to show the production of polythene as an example of polymerisation.
    (Lent by Imperial Chemical Industries Ltd.)
89. Examples of other plastics developed by I.C.I.
90. Faraday. Examples of platinum catalysts.
    (Lent by Royal Institution.)

91. Cavendish. Eudiometer.
(Lent by the University of Manchester.)

92. Calorimeter used for measurement of heat of adsorption of gases.
(Lent by Professor W. Garner.)

93. Photochemical apparatus, consisting of mercury lamp, filters, photochemical cell and photoelectric cell.
(Lent by Mr. E. D. Bowen.)

94. Exhibit on Chemical kinetics.
(Lent by Professor C. N. Hinshelwood.)

95. Photography. Development of photography in Great Britain.
(Exhibit arranged by Mr. A. Barclay from exhibits in the Science Museum collections and lent by Mr. G. H. Gabb and others.)

96. Development of cyanine dyes and their use in photography.
(Prepared by Kodak Ltd.)

97. Dixon. Photographic records of flames and explosions.
(Lent by the University of Manchester.)

98. Exhibit on flames and explosions, illustrating experimental technique.
(Lent by the Imperial College of Science and Technology, and Dr. D. T. A. Townend.)

99. Smithell's flame separator and other apparatus used in researches on flame.
(Lent by the Science Museum.)

100. Humphrey Davy. First safety lamps used in a coal-mine.
(Lent by the Science Museum.)

101. Explosives, illustrating methods employed in calorimetry, etc.
(Arranged by Sir Robert Robertson from exhibits lent by Woolwich Arsenal, the Museum collections and other sources.)

CHAPTER VI

VALENCY AND ATOMIC STRUCTURE

THE title of this chapter indicates the dual character of the development of our ideas of the nature and causes of the structures of molecules.

On the chemical side this began as soon as correct ideas of molecular sizes had been reached, which was just about the time when our Society was founded. The reactions of these molecules then led to the development of structural chemistry, which considered the order in which the atoms were linked rather than the nature of the forces which held them together, and the number of links that an atom could form, that is, the valency. This was the side with which the Society was mainly concerned.

Then, just about the turn of the century, beginning with the discovery of the electron by J. J. Thomson in 1897, the physicists started on the investigation of the structure of the atom itself ; the conception of the atom as a heavy nucleus surrounded by electrons (102) was put forward by Rutherford in 1911, and developed on the theoretical side by Bohr (1913). This enabled us to form an idea of the nature of the bonds of structural chemistry, but its application in detail to molecules of all kinds only became possible with the determination of the atomic number (Moseley, 1913–14) (113), which gave the compositions of the individual atoms.

Since then the chemical and physical sides of the problem have developed in constant correlation.

The chemical approach

The earliest work of importance is concerned with the fixing of the correct atomic weights (*e.g.* o = 16, giving H_2O instead of HO), which was a necessary preliminary to any true ideas of molecular structure ; this was achieved through the realisation of the difference between the atoms and the molecules of an element, and a recognition of Avogadro's principle. This took place mainly in 1850–60, and was largely due to the English chemists Edward Frankland, Buckton, and Odling ; they based their conclusions partly on vapour-densities (which, through their discovery of the volatile metallic alkyls could be applied to fix the atomic weights of the metals), and partly, especially with Odling, on general considerations of simplicity in organic equations (105). As soon as the true atomic weights and molecular compositions were known, the valencies of the elements were apparent ; the first statements along these lines were made by Frankland in 1852 (*Phil. Trans.*, 142), and the ideas were completed by the addition of tetravalent carbon by Kekulé in 1859.

In 1864 came Newland's Law of Octaves (103, 104), which, though it was not accepted, was the first real recognition of a periodic relation between atomic weights and chemical properties, a matter further discussed on p. 37.

In 1894 began the discovery of the rare gases, which were isolated essentially by chemical methods. The work has been described on p. 2, and in view of the immense importance of these elements in elucidating the relation between atomic number and chemical properties, and in completing the structure of the Periodic Table, it is noteworthy that they were all, including emanation (Rutherford and Soddy, *J.C.S.*, 1902) discovered by British workers.

Soon after this came the work of W. J. Pope and his collaborators which gave the first real evidence on the stereochemistry of elements other than carbon (nitrogen, 1899, 1901; sulphur, 1900; tin, 1900; selenium, 1902).

Of the later work bearing on molecular structure special mention should be made of that of G. T. Morgan and his collaborators on co-ordinated and especially chelate compounds; this provided a great deal of evidence in support and in extension of Werner's views on the structure of such compounds, especially of those formed by dyes with mordants. They also did much to develop and apply new and powerful co-ordinating agents such as dipyridyl (106).

The physical approach

On the physical side of the discovery of atomic structure most of the work was naturally not done by chemists and not published in the *Journal of the Chemical Society*, but there are certain points of special interest to chemists.

The first definite statement of the atomic nature of electricity, as a deduction from Faraday's laws, was made by Helmholtz in his Faraday Lecture (108) to the Chemical Society on April 5th, 1881 (*J.C.S.* **39**, 290).

The theory that radioactive change was due to actual atomic disintegration was put forward first by Rutherford and Soddy in the *Journal* in 1902 (**81**, 321, 837). The relation between electrons and valency was emphasised by J. J. Thomson in his Silliman Lectures (1903), and he gave an atomic model (*Phil. Mag.*, 1911) which suggested a reason for the periodic arrangement of the elements (112). The nuclear atom, the basis of all subsequent theories of valency, and of all subsequent investigations of atomic structure, was proposed by Rutherford in 1911. The radioactive displacement law, which threw so much light on the relation between atomic constitution and position in the Periodic Table, was put forward independently in 1913 by Fajans, A. S. Russell, and Soddy. Its establishment was mainly due to work on the chemical nature of radioactive products carried out by Fleck (*J.C.S.*, 1913) under Soddy's direction (109).

The discovery of isotopes is due to Soddy, who began to discuss these in 1910; he invented the name, and by 1913 had the idea complete. His determination of the abnormal atomic weight of lead from thorium (110), which may be called the first experimental proof of the existence of isotopes, is in the *J.C.S.* for 1914. The work of Aston, carried out by the aid of his invention, the mass-spectrograph, gave us an extensive knowledge of the isotopic constitution of the elements, as well as highly accurate values for many atomic weights.

Moseley's work on the X-ray spectra of the elements (113), and his deduction from it of the atomic number (*Phil. Mag.*, 1913–14), first gave what may be called the composition of the atoms, and enabled the relation between this and the chemical properties to be worked out.

Finally, the paper by C. R. Bury (111), a Fellow of the Chemical Society, which corrected Langmuir's distribution of the electronic groups in an atom, and was a very valuable contribution to atomic structure, was based entirely on chemical properties (*J. Amer. Chem. Soc.*, 1921, **43**, 1602).

APPLICATIONS OF QUANTUM THEORY TO CHEMISTRY

Undoubtedly the greatest single work in existence on the application of quantum theory to chemistry is the treatise on Statistical Mechanics by Fowler. This book has exercised a dominating influence on all workers in the field and contains the germs of many subsequent advances. The groundwork was laid here for the development of quantum statistical theories of the gaseous, liquid and solid states, and for much of the newer chemical thermodynamics. Thus the work of Guggenheim on the electrolytes and on adsorption might be instanced as a direct outcome of Fowler's pioneer investigations in these fields.

In 1929 Lennard-Jones in a classical paper introduced the idea of molecular orbitals, so laying the foundation of a powerful method for calculating the electron-configuration of polyatomic molecules. The electronic structure of the double bond, of the benzene molecule and more generally of molecules for which no single classical structural formula can be written (*i.e.* molecules with mesomeric or resonating structures) have all been clarified by the orbital method. Penney has applied both the ' election-pair ' method of Pauling and the ' orbital ' method of Lennard-Jones to a number of simple polyatomic molecules. In particular Penney and his co-workers have explained the reason why benzene occupies a peculiar position in the series of cyclic hydrocarbons (*i.e.* the distinctive property of aromatic character), the peculiar unsymmetrical structure of hydrogen peroxide and hydrazine, and the intermediate bond lengths in many mesomeric structures.

Lennard-Jones and his co-workers have developed the first quantum theory of the interaction of atoms with solid surfaces, giving a theoretical derivation of the constants in the Langmuir isotherm. They have also been able to explain the anomalous scattering of beams of helium by crystals of lithium and sodium fluoride, found in the experiments of Frisch and Stern. Among the other valuable information which this elegant treatment gives we might instance the average length of time spent by an adsorbed atom on the surface and the energy-levels of the adsorbed atom, both of fundamental importance in any theory of surface catalysis.

The application of the quantum theory to chemical reactions was initiated by Polanyi in a fundamental paper with Eyring in 1931 (*v.* p. 22). It was there shown how the activation energy of certain simple chemical reactions could be calculated from a knowledge of the physical properties of the reactants. The resulting conception of an activated complex in the transition state from the reactants to the reaction products has proved of immense value in the general theoretical interpretation of chemical reactivity. The theory of Eyring and Polanyi has been further developed by Bell and by Lennard-Jones and Strachan.

One of the most interesting and practical applications of quantum theory to chemistry is that made by Gurney and Mott, who provided the first satisfactory theory of the latent image in photography. They have been able to show why it is essential to have traces of impurity (silver sulphide) in the silver halide lattice in order to get sensitivity, how the developer distinguishes between exposed and unexposed grains of silver halide and to explain many of the complex phenomena associated with the photographic process.

EXHIBITS

Valency and Atomic Structure

102. Bohr-Rutherford atom.
(Lent by the Science Museum.)

103. Newlands' Law of Octaves.
(Lent by the Science Museum.)

104. Spiral illustrating the genesis of the elements. (Prepared by Sir William Crookes.)
(Lent by the Science Museum.)

105. Frankland's organo-metallic compounds.
(Lent by the University of Birmingham.)

106. Sir Gilbert Morgan's chelate compounds.
(Lent by the Chemical Research Laboratory, Teddington.)

107. Copy of ' The Electronic Theory of Valency,' by N. V. Sidgwick.

108. Copy of Helmholtz' Faraday Lecture.

109. Diagram of disintegration series of the radio elements.
(Prepared in the Science Museum from information supplied by Professor F. Paneth.)

110. Lead isotope, prepared from thorite.
(Lent by Professor Soddy.)

111. Bury's paper in *J.A.C.S.* correcting Langmuir's distribution of electronic groups in an atom.
(*J. Am. Chem. Soc.*, 1921, **43**, 1602.)

112. J. J. Thomson's apparatus for weighing the electron.
(Lent by the Science Museum.)

113. Moseley's apparatus and ferrocyanide crystals.
(Lent by the Museum of the History of Science, Oxford.)

CHAPTER VII

INORGANIC CHEMISTRY

GENERAL CONSIDERATIONS

TO inorganic chemistry belongs the pride of being the oldest and first developed field of chemistry. The fundamental developments lie before 1841 during the period of Cavendish, Priestley, Black, Davy and Dalton, the century when the commoner elements were discovered and the foundations of modern chemistry were laid.

Consequent on the rapid advance and relative prominence of organic chemistry, particularly in the latter half of the nineteenth century, other branches of the science suffered some eclipse, and particularly inorganic chemistry. It seemed to assume the role of a completed science, in which advances were limited to refinements of analytical technique and the discovery of new elements rather than the discovery of new principles. It was not until physico-chemical principles and methods were applied that inorganic chemistry again began to develop and ramify during the first half of this century into what are now often regarded as new branches of physical chemistry.

The story is thus not one of continued and steady progress, but rather one of decline followed by new development and interest. On the other hand, the last hundred years has seen the vast and steady development of inorganic chemical industry from very simple beginnings, such as are typified by our old alum industry (119). The difficult and hazardous beginnings of what are now great inorganic chemical industries are well illustrated by the process, used first in Great Britain by the Alliance Aluminium Co. at Wallsend-on-Tyne, for producing metallic aluminium by plunging a ball of metallic sodium into a bath of molten cryolite.

By 1840 Dalton's Atomic Theory was well established, but considerable confusion persisted because there was no sound and accepted system of atomic weights (114). When in 1858 Cannizzaro drew attention to Avogadro's Hypothesis and showed how it could be applied to establish a logical system of atomic weights he laid the foundation for the Periodic Classification of the elements upon which subsequent developments have largely depended.

PERIODIC CLASSIFICATION

The periodic classification stimulated much of the work done by inorganic chemists from the latter part of the nineteenth century. J. H. Gladstone recognised, as early as 1853, that the atomic weights of similar elements might be related in three ways :—

(*a*) They might be nearly the same, *e.g.* Co and Ni.

(*b*) They might be in multiple proportion, *e.g.* Pd (53·3), Pt (98·7), and Au (197).

(*c*) They might differ by a common increment, *e.g.* Li, Na, and K.

Odling, in 1857 and 1864, published a classification of the elements into thirteen groups essentially triads. He noticed marked continuity when elements were arranged in numerical order of atomic weights and also that similar elements are frequently separated by intervals of 48, also 44, 40 and 16, which led him to believe that 4 might represent a fundamental unit of common difference.

The 'Law of Octaves' proposed by Newlands in 1865 was an anticipation of the later classifications of Mendeléeff and Lothar Meyer, but he left no gaps for missing elements and his idea did not receive the attention it deserved.

H. G. J. Moseley, 1913–14 (113), studied the X-ray spectra of elements and was able to assign an atomic number to each element (p. 33). Using atomic numbers instead ot atomic weights the anomalies in Mendeléeff's classification disappeared, and the number and the place of the rare earths in that system was established. Aston's study of the isotopic constitution of the elements completed our knowledge of these anomalies.

DISCOVERY OF ELEMENTS

In 1861 Crookes announced the discovery of thallium (116) and in 1900 also of uranium X.

The work of Rayleigh, Ramsay, Travers, Rutherford, Soddy and Whytlaw-Gray, in the discovery of a completely new group of unique chemical elements, the inert gases, has been described in Chapter I (p. 2).

Beside the discovery of radon in this group we may note that Rutherford and Soddy discovered thorium X in 1902, and Soddy and Cranston, in 1918, discovered protoactinium independently of Hahn and Meitner.

The subsequent discovery and isolation of isotopes, arising mainly from the work of Rutherford, Soddy and Aston, lies on the borderline of physics and chemistry, but the utilisation of isotopes as tracer elements is leading and will lead to great advances in chemical knowledge.

ADVANCES IN GENERAL INORGANIC CHEMISTRY

A considerable volume of knowledge of inorganic chemistry has accumulated from the small contributions of chemists too numerous to mention here, and an illustration of this occurs in the chemistry of one element, not itself a British discovery, viz. iodine (124).

The precise determination of atomic weights has occupied the attention of many inorganic chemists throughout the last hundred years, among whom be mentioned T. E. Thorpe (Ti, Si, Au), Burt and Edgar (H = 1·00772), and more recently H. U. A. Briscoe (Sn, V, Tl, B, Br, Si) leading to work on isotope separation and isotopic exchange reactions. The development of the gas density microbalance by R. Whytlaw-Gray and his collaborators contributed materially to the accurate determination of the molecular weights of gases and has been applied particularly to the evaluation of the atomic weights of the inert gases and of carbon.

Among substantial contributions in inorganic chemistry we may single out the following :—

E. Frankland, 1848–99, in his attempt to isolate the organic radicals discovered zinc alkyls, leading to his well-known researches into many previously unknown organo-metallic compounds.

Roscoe, 1854–1915, made valuable contributions to inorganic chemistry, the most important of which was without doubt the establishment of vanadium as a tri- and penta-valent element of the phosphorus group, and the isolation of the metal for the first time (115). He made valuable contributions to the chemistry of the halides of other multivalent metals, particularly tungsten, uranium and niobium, and first described UCl_5, $NbCl_3$, and $NbOCl_3$.

Crookes, 1851–1919, made the most valuable of his many contributions to inorganic chemistry by his expert knowledge of spectra, leading to the discovery of two new elements and development of special glasses opaque to infra-red and ultra-violet light (122).

T. E. Thorpe, 1865–1925, ranged over a wide field of chemistry, but is best known in inorganic chemistry for his reasearches into phosphorus and fluorine compounds. His discovery and determination of the vapour-density of PF_5 placed the quinquevalency of phosphorus beyond doubt, and his investigation of the vapour-density of hydrogen fluoride, showing that it gradually diminished between 26° and 88° C., proved the correctness of the formula HF (117). He made a thorough investigation of phosphorus tetroxide and trioxide, obtained by burning phosphorus in a limited supply of air.

L. Mond, 1890–1909, discovered nickel carbonyl, the first of a unique series of metal compounds. He followed this by a study of iron, cobalt, molybdenum and ruthenium carbonyls. His greatest attainments lay, however, in industrial chemistry and his well-known process for the refining of nickel, based on his discovery of the carbonyl, which remains unchanged except in detail to the present day, also supplies us with many rare and useful metals of the platinum group (125).

Shenstone, in 1901, found that pieces of quartz fused together in an oxyhydrogen flame could be worked like glass yielding vesssels remarkably resistant to temperature change thus laying the foundation of an industry in fused silica ware, now supplemented by fused alumina ware (120).

Active nitrogen, the exact nature of which is still the subject of discussion, was discovered in 1911 by the present Lord Rayleigh.

The rise of modern inorganic chemistry received its impetus from the co-ordination theory of Werner and was greatly accelerated in 1923 by N. V. Sidgwick's modernisation of the theory in terms of the electronic theory of valency (107), which has resulted in the investigation of co-ordination complexes of elements of every group of the Periodic Table. Interest has largely centred on the structure and configuration of complex compounds and the work of all British chemists in this field has been closely interrelated. The theoretical implications are discussed in the section on Valency and Atomic Structure, Stereochemistry, and the Crystalline State, and only a short account of the additions to our knowledge of inorganic chemistry will be given here.

Two of the earliest British workers in this field were G. T. Morgan and N. V. Sidgwick. The former, who was inspired by Werner's view that the lakes of mordant dyes were internal metallic complexes, made a special study of co-ordination by polyfunctional groups, particularly acetylacetone and di- and tri-pyridyl. Our word *chelate* was his suggestion. He used strongly co-ordinating chelate groups to stabilise a number of elements in their less usual valency states, for example, cuprous salts and salts of divalent silver (106). His contribution to the extraction of the rare elements germanium, gallium and rhenium from British sources is also well known. Sidgwick is pre-eminent for his contributions to valency theory. In the experimental field his discovery and investigation of the first known co-ordination complexes of the alkali metals (1925) and later of thallium gave important substantiation to that theory.

From 1931 onwards C. S. Gibson, who had prepared diethylmonobromgold with Pope in 1907, made a thorough study of tervalent gold compounds, established the uniform tetracovalency of tervalent gold and produced positive evidence of the halogen bridge between gold atoms (121).

Although Werner's view that platinous complexes have a planar configuration had been generally accepted, there was an immediate revival of interest in 4-co-valent complexes when Drew, in 1929, showed that the supposed *cis-* and *trans-* forms of Me_2TeI_2 were structural isomers, and thought was stimulated in this field by the theoretical predictions of Pauling. Nickel, palladium, platinum and copper complexes were especially studied ; and by an investigation of their reactions, their isomerism and, most important of all, by X-ray structure determinations, particularly by E. G. Cox, Drew, F. G. Mann, W. H. Mills, S. Sugden, W. Wardlaw and their collaborators, it was shown that both planar and tetrahedral distribution of valencies occur, depending on the central element in the complex and its principal valency, according to Pauling's predictions.

Mann prepared the second known purely inorganic optically active complex $Na[Rh((NH)_2SO_2)_2 2H_2O]$ (1933) and demonstrated that the parachor could not be used as a guide in the determination of the structure of complex salts. His more recent contribution to the chemistry of bi- and poly-nuclear complexes of various metals with organic arsines and phosphines, in which he established the existence of the halogen bridge between the metal atoms and studied the chemical reactions of bridged complexes, are also well known.

Comparatively recently the chemistry of covalent fluorine compounds has aroused world-wide interest both in the academic and industrial fields, a notable contribution coming from H. J. Emeléus in the preparation and characterisation of a number of alkyl and aryl substituted fluorides of silicon, sulphur, selenium, tellurium and iodine (117).

Apart from this study of co-ordination chemistry is the examination of phase relationships of mixed salt solutions by H. Bassett and the conductometric studies of precipitation by H. T. S. Britton.

EXHIBITS

Inorganic Chemistry

114. John Dalton. Pictures, documents and apparatus.
(Lent by the University of Manchester, Mr. G. H. Gabb and others.)

115. Sir Henry Roscoe. Illustrating his researches on the vanadium compounds.
(Lent by the University of Manchester.)

116. Thallium. Original thallium compounds, 1862. Laboratory notebook of Sir William Crookes.
(Lent by the Science Museum.)

117. Fluorine. Exhibit of development and practical applications.
(Prepared by Imperial Chemical Industries Ltd.)

119. Alum. Production of alum illustrated by column of crystals.
(Lent by Peter Spence & Sons Ltd.)

120. Fused silica and alumina. Production of fused vitreosil, pure fused silica and fused quartz.
(Lent by the Thermal Syndicate Ltd.)

121. (*a*) Extraction and refining of precious metals. Developments in the preparation of the metals and their industrial applications.
(Prepared by Johnson Matthey & Co. Ltd.)

(*b*) Gold compounds and thin gold films.
(Lent by Professor C. S. Gibson.)

122. Glass. The development of special glasses.
(Prepared by Chance Bros. Ltd.)

123. Fluorescent lighting. Development, properties and applications of luminescent materials.
(Prepared by the General Electric Co. Ltd.)

124. Iodine. Comprehensive exhibit on chemistry and applications of iodine.
(Prepared by the Iodine Educational Bureau.)

125. Nickel and carbonyls. Historical developments in the production of nickel and carbonyls.
(Prepared by the Mond Nickel Co. Ltd.)

126 Metallurgical exhibits. Historical developments in the metallurgy of iron and steel.
(Arranged by Dr. C. H. Desch from exhibits supplied by Samuel Osborne & Co., the Royal Mint, the University of Cambridge and other sources.)

CHAPTER VIII

AGRICULTURAL CHEMISTRY

THE early books of Davy (1813) and Liebig (1840) served to focus discussion on possible applications of chemistry to agriculture, but they lacked a basis of firmly established facts. These first began to emerge from experiments actually conducted in the field and followed by careful chemical analyses of the soils and produce. Such experiments were first made by J. B. Boussingault (1834) in France, and J. B. Lawes (1839) on his Rothamsted estate at Harpenden, Hertfordshire. Lawes discovered that the phosphate in bones and rock phosphates could be converted into a much more active fertiliser by treating them with sulphuric acid to form the water-soluble salt, then called ‘ superphosphate of lime.’ He took out his patent in May, 1842, and started the first fertiliser factory at Deptford. In the following year he embarked, with the aid of J. H. Gilbert, on a series of field experiments to test the effect of farmyard manure and a variety of salts on crops grown every year on the same land. Lawes and Gilbert worked together until 1900 and some of their original experiments are still continued. Typical produce from the Broadbalk wheat experiment in its centenary year are exhibited (127).

The Rothamsted work soon demonstrated the great value of nitrogen manures, especially ammonium and nitrate compounds, and thus prepared the way for the establishment of a fertiliser industry based, first, on natural materials or industrial by-products and, then, on compounds synthesised from the nitrogen in the air.

Working at Rothamsted, R. Warington, the son of one of the founders of the Chemical Society, studied the formation of nitrate in field soils and its loss by drainage. He was able to show that one group of bacteria oxidised ammonium to nitrite and another group completed the oxidation to nitrate. His work prepared the way for the development of soil microbiology.

In a very carefully controlled series of pot experiments Lawes and Gilbert (1861) showed that green plants were unable to utilise the nitrogen of the atmosphere. They had excluded contamination so strictly that they had kept out the bacteria subsequently (1888) found by two German chemists to be responsible for the fixation of atmospheric nitrogen in the root nodules of clovers and other leguminous plants. This discovery showed one of the ways in which soil fertility may be restored when land is rested under natural vegetation or under cultivated mixtures of grasses and clovers.

Practical observations that a column of soil could deprive urine of its colour and smell and remove ammonia from solutions of its salts led J. T. Way (1850) to an important investigation on the power of soils to absorb manure. He showed that lime is liberated when ammonia is absorbed and thus established the general phenomenon of ' base-exchange ' which has since been made the basis of important analytical methods and industrial processes for softening waters and purifying a vast variety of materials.

As early as 1845 Daubeny, at Oxford, made field experiments on different crop rotations and drew a distinction between ' active ' and ' dormant ' plant nutrients in the soil. In 1894 Dyer showed that citric acid provided a convenient reagent for determining the amounts of plant foods in soils which were probably available to plants. His method is still widely used and a large number of more rapid approximate methods have since been developed for analysing both soils and plants.

Field experiments parallel to those at Rothamsted began on a light soil at Woburn, Bedfordshire, in 1876. By the end of the century plots with sulphate of ammonia became infertile and were found to be acid to litmus paper. They were restored to fertility by dressings of lime. This striking demonstration and the development of more precise methods of measuring soil acidity have led in recent years to a long overdue revival of the old practice of systematically liming many classes of land.

Lawes and Gilbert carried out fundamental experiments on animal feeding and made detailed dissections and chemical analyses of a large number of experimental animals. They established the fact that animals can build up fats from carbohydrates and demonstrated the importance of proteins and mineral elements in the feeding of animals.

A valuable little book by R. Warington entitled *The Chemistry of the Farm* ran through many editions and did much to determine the pattern of future text-books and investigations on agricultural chemistry. His book on *The Physical Properties of the Soil* prepared the way for modern developments in soil physics.

The developments described in this chapter are largely illustrated by Exhibit No. 127, prepared and lent by the Rothamsted Experimental Station.

CHAPTER IX

ORGANIC CHEMISTRY AND BIOCHEMISTRY

THE history of organic chemistry in this country can be traced back to the early days of the nineteenth century. In 1803 Dalton used explosive combustion with oxygen to analyse volatile organic compounds, and his subsequent atomic theory provided a quantitative basis for further developments. It is to Faraday, in 1825, that the discovery of benzene in ' oil-gas ' is attributed (156, 157), and in the following year he prepared two naphthalene-sulphonic acids, which were the first true representatives of this important class of compound. It is not improbable that in the discovery of benzene he may have been anticipated by Accum who, working in the Surrey Institution, described in 1819 various by-products obtained in the manufacture of coal gas, including the ' Highest Rectified Essential Oil,' which must have consisted largely of benzene (155).

Dyestuffs and colouring matters

The study of the coal tar hydrocarbons (158) by Hofmann and Mansfield in the years 1845–50 at the Royal College of Chemistry, London, helped to lay the foundations of aromatic chemistry, and a process was patented for nitrating benzene to give nitrobenzene, from which Hofmann (164) prepared the aniline which he used in his subsequent investigations on alkylated anilines. m-Nitraniline was prepared for the first time from m-dinitrobenzene by Hofmann and Muspratt in 1845. These investigations paved the way for the preparation of the first synthetic dyestuff, ' Mauve,' by Perkin, in 1856, by the oxidation of aniline with bichromate and sulphuric acid (162). This was followed by its production on a manufacturing scale, which involved the elaboration of manufacturing processes for nitrobenzene and aniline in addition to the introduction of new methods of applying the new colouring matter to textiles. In this way the foundation of the Coal Tar Colour Industry was laid. Perkin also invented the use of tannin with a metallic mordant for the application of basic dyes to cotton and discovered the first azo-compound, aminoazonaphthalene. Simultaneously with Graebe and Liebermann he showed how anthraquinone could be converted into alizarin—

the first synthesis of a natural dyestuff—and later manufactured alizarin from *meso*-dichloroanthracene. Among subsequent developments in this field may be mentioned Nicholson's manufacture of magenta in a crystalline form in 1862, and his discovery of the phenylated rosanilines, Alkali Blue and Soluble Blue, the first synthetic acid wool dyestuff. At about the same time Greville Williams discovered Quinoline (or Cyanine) Blue and Safranine T, and Griess, working at Burton, discovered the diazo compounds and many of their reactions, which led to the introduction of azo dyestuffs. The first successful azo dye, Bismarck Brown, was made in Manchester by Caro and Martius, who also produced Induline and Martius (or Manchester) Yellow (1864). Witt, whilst in England, discovered phenosafranine and the Tropaeoline dyes, and put forward the chromophore-auxochrome theory of colour which resulted in important theoretical developments (1876). At about this time the initiative in dyestuffs research passed from this country, although a few investigators carried on the tradition. In 1879 Meldola discovered the first oxazine dye—Meldola's Blue—and carried out important investigations on diazo- and diazoamino- compounds (163). The thiazole dyestuff, Primuline, was discovered by Green in 1887, which introduced the process of developing dyestuffs on the fibre. He also made other important contributions on the stilbene dyes and on Aniline Black. In the period 1880–1900 the work of Armstrong and Wynne on naphthalene chemistry was of the greatest importance for the development of dyestuffs-chemistry and Armstrong's quinone theory of colour (1888) became a guiding principle (159).

The war of 1914–18 brought about a revival of interest in dyestuffs in this country, and great technical advances have been made since that time. The constitution of photosensitising dyes such as pinacyanol was investigated by Mills and (Miss) Hamer, who have made important contributions in the field of the polymethine dyes. Piggott and Rodd introduced the use of diarylformamidines in the synthesis of these dyes, and Morgan, and later, Drew advanced our knowledge of the metal complexes of mordant dyestuffs. Of new dyestuffs, Caledon Jade Green, a vat dyestuff of the dibenzanthrone series, discovered by Davies, Fraser-Thomson and Thomas in 1920, is outstanding on account of its wonderful fastness, and an entirely new class of pigment was discovered in the phthalocyanines, the structures of which were established by Linstead (165). Copper phthalocyanines furnish the fastest known blue and green pigments. Many new dyestuffs were invented with the introduction of acetate rayon, and among these may be mentioned the Ionamine dyes of Green and Saunders, the dispersed aminoanthraquinones of Baddiley and Shepherdson, and the sulphoricinoleic dispersed dyes of Ellis (166).

Theoretical Organic Chemistry

In the year 1849 Frankland claimed to have prepared free methyl by heating methyl iodide with zinc, but Schorlemmer, at Manchester, where he later occupied the first Chair in Organic Chemistry in this country, showed that the supposed radical was in fact a molecule, and that the radical twin of methyl was the hydride of ethyl. The contributions of Frankland, however, not only provided some of the earliest examples of organo-metallic compounds of the type which later workers developed with such success for synthetic methods, but also furnished valuable new conceptions to the then new subject of valency (105).

Notable contributions have been made to our knowledge of the subject of stereochemistry. The resolution of ammonium, sulphonium, selenonium and stannic compounds into optical antipodes by Pope (1899–1902) showed for the first time that optical activity could arise from the presence of asymmetric atoms of elements other than carbon (130). In 1909 Pope and Perkin (junior) synthesised and resolved methyl*cyclo*hexylideneacetic acid, thus providing the first experimental proof that optical activity does not require the presence of an asymmetric atom, but is a consequence of the dissymmetry of the molecule as a whole. The discovery that certain substituted diphenic acids could be obtained in optically active forms was made by Christie and Kenner in 1922, while the discovery of optically active sulphinic esters by Phillips in 1925 showed the previously unsuspected non-planar configuration of the sulphinic acid group. This led to the preparation of optically active sulphoxides by Kenyon and Phillips in 1926. Notable contributions to the stereochemistry of sulphur compounds were also made by Bennett. Similar studies with tellurium were made in 1929 by Lowry and Gilbert. Many further examples of optical activity due to molecular dissymmetry were provided by Mills, who was also responsible in 1920 for the first example of an optically active axially symmetrical spirocyclic compound. The long outstanding problem of the configuration of allene was solved by Maitland and Mills in 1936 by the preparation of the highly optically active and stable enantiomorphous forms of diphenyldinaphthylallene. In the development of the stereochemistry of compounds which give rise to optical activity as a result of restricted rotation valuable contributions were made by Mills, Kenyon, Bell and Turner. Much pioneer work has also been carried out on the stereochemistry of metallic compounds. An optically active arsenic compound was prepared by Mills and Raper in 1925, and many notable advances on the stereochemistry of metallic co-ordination compounds have been reported by Mann, Morgan and Mills. The achievement of the first undisputed asymmetric synthesis must be attributed to McKenzie (1904), who made many contributions to the stereochemistry of intramolecular change. Pickard and Kenyon have greatly extended our knowledge of optically active alcohols, and Kenyon and Phillips, and latterly Ingold and Hughes, have made valuable contributions to the elucidation of the Walden inversion. Pioneer work on organic derivatives of silicon was carried out from 1901 onwards by Kipping, who, in 1907, prepared an optically active compound containing an asymmetric silicon atom (128).

Important contributions to the subject of tautomerism were made by J. F. Thorpe, in collaboration with Kon, Farmer and Linstead. Mention must also be made of the fundamental investigations on the mechanisms of organic reactions which have been carried out by numerous workers. The application of the Ionic Dissociation Theory of Arrhenius to the reactions of organic compounds was first visualised by Lapworth in 1903, and his many later contributions, together with those of Robinson and Ingold, led ultimately to the important Electronic Theory of Organic Reactions. Important contributions on the subject of organic reactions involving free radicals and atoms have been made by Hey and Waters.

Terpenes

Tilden was one of the earliest workers in the terpene field. His observation that many terpenes could be characterised by the formation of crystalline nitrosochlorides was a discovery of far-reaching importance. Henderson carried out many fundamental investigations into the chemistry of pinene, camphene and borneol. The work of Perkin (junior) on the synthesis of terpenes and their degradation products was an outstanding contribution. This tradition was maintained by Simonsen, who made valuable contributions to the chemistry of both the mono-terpenes, piperitone, thujene, the carenes, angustione and others, and the sesquiterpenes such as cyperone, eremophilone, the caryophyllenes, santalols and curcumenes. Important fundamental investigations on the stereochemistry of the menthols and related compounds have been made by Read. Mention must be made of the synthetic work of R. D. Haworth related to deterpenes, and in the difficult field of triterpene chemistry the contributions of Heilbron, Spring, Kon and Simpson have been of particular importance (131).

Isoprene was first isolated by the destructive distillation of rubber by Greville Williams in 1860, and the same hydrocarbon was later prepared by Tilden (1884) by pyrolysis of turpentine. Tilden showed the relationship between natural rubber and isoprene, and in 1891 he prepared the first synthetic rubber when he showed that isoprene prepared from turpentine is converted into a rubber-like material on standing or under the influence of hydrochloric acid (168). He also was the first to use sulphur for the vulcanisation of synthetic rubber. Matthews and Strange introduced in 1910 the use of metallic sodium for the polymerisation of dienes to synthetic rubbers, and in the years 1909–14 with Perkin (junior) and Weizman several new routes for the synthesis of dienes were developed (169).

Oils and fats

Important investigations have been made in the chemistry of oils and fats by Hilditch and by Francis and Malkin. While the latter workers have synthesised many individual simple and mixed triglycerides, Hilditch, working on a wide variety of natural oils and fats, has been able to classify them according to their compositions, and has shown how these are related to the organism and its place in the evolutionary system (145).

Carbohydrates

Outstanding contributions of the greatest importance have been made in the carbohydrate field. Reference may be made to the early work of Schunck, O'Sullivan and Brown on the chemistry of the polysaccharides and gums, but it was the pioneer work of Purdie at St. Andrews in the early years of the century on the methyl ethers of sugars which prepared the way for an entirely new chapter in the structural chemistry of the carbohydrates. This line of work was developed by Irvine, who applied it to structural problems in both the monosaccharide and the polysaccharide field. In the same laboratories W. N. Haworth (Nobel Laureate) first obtained evidence of the mode of linkage in the disaccharides, and Hirst provided in 1923 the first proof of the presence of the pyranose ring in a normal methyl-xyloside by a general method which was later applied to numerous other sugars. In the same year Pryde provided evidence of the pyranose ring in the case of the hexose galactose. The existence of the furanose ring in a γ-derivative of galactose was first demonstrated by Haworth in 1924, and in 1926 Haworth and Hirst showed the presence of the furanose structure in the fructose component of sucrose. Rapid developments in the fundamental structural chemistry of the carbohydrates came from St. Andrews under Irvine (134), and from Birmingham under Haworth and Hirst, which rendered possible for the first time the extension of constitutional investigations to the much more complex field of the polysaccharides. The mode of linkage of the sugar residues was determined for starch, glycogen, cellulose, inulin and more recently by Stacey for certain important bacterial polysaccharides. The Birmingham laboratories were also responsible in 1928 for the introduction of the ' end-group ' method of assay, which has given an insight into the molecular architecture of the polysaccharides and the complex plant and animal gums and mucilages (136). The determination of the structure of glucosamine was achieved independently by Peat using chemical methods and by Cox by means of X-ray crystallography. Important discoveries in the enzymic chemistry of the starches and dextrins, including the synthesis of both amylose and amylopectin from glucose-l-phosphate, have been made by Hanes (1940) and by Peat (1945). Reference should also be made to the work of Robertson on ethylene oxide ring derivatives, to the synthesis of the crystalline *iso*-sucrose by Irvine and Oldham in 1929, and to the important studies of Lowry on the mutarotation of glucose. Outstanding achievements on the industrial side were Mercer's contributions to the chemistry of cellulose, the discovery of xylonite (celluloid) and its subsequent manufacture by Parkes in 1877 (170), who found that camphor could be used as an effective plasticiser with the lower nitrates of cellulose, and the discovery of the viscose process (137-9) for the manufacture of artificial silk introduced by Cross and Bevan in 1892. In the biochemical field fundamental observations were made by Harden (Nobel Laureate) on yeast fermentation. He established the function of phosphates in the fermentation of sugars and isolated hexosediphosphate (135). He also demonstrated for the first time the presence of a co-enzyme as an essential agent in enzymic processes. Robison was responsible for the characterisation of many of the products of carbohydrate metabolism. He isolated and identified many hexose phosphates and made fundamental contributions to our knowledge of the chemical mechanism of bone formation.

Natural colouring matters

Mention must be made of the contributions made by (A. G.) Perkin to the chemistry of the natural colouring matters related to flavone, and of the later work of Robinson on the anthocyanins, the colouring matters of flowers and fruits. A new method for the synthesis of flavones and flavonols was developed by Robinson and applied to chrysin, fisetin, quercetin, and morin. The first reported synthetic route to an anthocyanidin is due to Everest (1914) and later improved methods were developed by Robinson and applied to cyanidin, pelargonidin and delphinidin chlorides, the colouring matters of the deep-red chrysanthemum, the purple-red aster and the delphinium respectively. These syntheses, achieved without the use of the more drastic reactions used by earlier workers, placed the structures of the anthocyanidins on a sure basis. The positions of the sugar groups in the natural anthocyanins were also elucidated by Robinson, and with Robertson he synthesised in 1928 the first actual flower pigment, callistephin. Similar syntheses of chrysanthemin, oenin, pelargonin, cyanin, peonin and malvin followed.

Amino-acids and related compounds

Thudichum, who settled in England in 1853, is regarded as the father of British biochemistry, and he made many outstanding contributions to the chemistry of the pigments of urine, bile and blood, and laid the foundation of our knowledge of the chemistry of the brain, from which he isolated kephalin, sphingomyelin, phrenosin and kerasin and, as cleavage products, galactose, sphingosine, aminoethyl alcohol and neurostearic acid (144). The amino-acid tryptophane was discovered in 1901 by Gowland Hopkins (Nobel Laureate), who later discovered the important tripeptide, glutathione. Histidine was synthesised by Pyman in 1916. Mention must also be made of the synthesis of thyroxine by Harington in 1927, who had proposed the correct formula in the previous year ; and in 1935 Harington achieved the synthesis of glutathione (141). Chibnall was responsible for the development of precise chemical methods for the characterisation of proteins by means of amino-acid analysis, and more recent novel contributions to this subject have been made by Martin and Synge. Extensive researches on the biochemistry of lower fungi or moulds were carried out by Raistrick, who isolated a number of metabolic products and determined their structure by synthesis.

Hormones and carcinogenic hydrocarbons

In 1929 Marrian first isolated pregnanediol, the metabolic product of the hormone of the *corpus luteum*, from human pregnancy urine and characterised it as a saturated diol. Œstriol, one of three closely related œstrogenic substances present in human pregnancy urine, was first isolated by Marrian in 1930 and characterised as a phenolic tetracyclic triol and in 1932 he showed that on fusion it gave a phenolic dicarboxylic acid (since given the name marrianolic acid), which proved to be of considerable importance in the elucidation of the structures of the whole group of natural œstrogens (149). The non-specificity of the œstrogenic response was recognised in 1933 by Cook, Dodds and Hewett, who showed that such action could be produced by a wide variety of organic compounds. This work led Dodds, in collaboration with Robinson, to the synthesis of a number of highly active artificial œstrogens, such as stilbœstrol (1938), hexœstrol and dienœstrol (150). These compounds have the same order of potency as the natural hormone, and in addition are active when given by mouth ; they are also being used, with very satisfactory results, in the treatment of prostatic cancer.

Potent cancer-producing tars were prepared by Kennaway in 1924 by the pyrogenic decomposition of pure hydrocarbons, and in 1930 he showed that 1:2:5:6-dibenzanthracene was a carcinogenic compound of moderate potency. This was the first pure compound shown to have this property. A large number of carcinogenic hydrocarbons were synthesised by Cook (1930–39), many of which were highly active. These were related to 1 : 2-benzanthracene, the fluorescence spectrum of which had been previously shown by Mayneord and Hieger to be similar to that of crude cancer-producing tars. The potent cancer-producing hydrocarbon 3 : 4-benzpyrene was isolated from coal-tar pitch and synthesised by Cook, Hewett and Hieger in 1932. In 1934 Cook and Haslewood demonstrated the carcinogenic activity of methylcholanthrene, a derivative of the bile acids.

Alkaloids

During the past century more than ninety new alkaloidal bases have been isolated by investigators in this country, and some of these are now of pharmacopœial importance. Among the ergot alkaloids ergotoxine was first isolated as the crystalline phosphate by Barger and Carr in 1906, and first crystallised as base by Smith and Timmis in 1930, who also isolated ψ-ergotinine. The same workers were the first to isolate ergosine and ergosinine in 1937. Ergometrine was isolated by Dudley and Moir in 1935. The bases tyramine and histamine were found in ergot by Barger and by Barger and Dale (Nobel Laureate) in 1909 and 1910 respectively. Of the ipecacuanha alkaloids Paul and Cownley were the first to separate emetine, cephaeline and psychotrine in the pure state between 1894 and 1898. In 1917 Pyman isolated emetamine and O-methylpsychotrine. The inter-relationship between these alkaloids was established by Carr and Pyman. Among the jaborandi alkaloids pilocarpine was first prepared by Gerrard in 1875, and the subsidiary alkaloid pilosine was discovered and its constitution established by Pyman in 1912. d-Tubocurarine chloride, one of the curare alkaloids, which secures relaxation of muscles in anæsthesia, was first isolated in the crystalline state from tube-curare by King in 1935, who showed its relationship to bebeerine (curine) (133). King later isolated l-tubocurarine chloride from *Chondrodendron tomentosum*, and a new alkaloid, neoprotocuridine, was isolated from pot curare. Digoxin, used in the treatment of cardiac disorders, was first isolated by Smith in 1930 from *Digitalis lanata*. Notable contributions have also been made to the synthesis of alkaloids and to the elucidation of the most involved alkaloidal structures. Particular mention must be made of the interesting syntheses of tropinone (1917) and pseudo-pelletierine (1924) due to Robinson, and of the synthesis of narcotine by Perkin and Robinson in 1911. In collaboration with Perkin and Clemo, Robinson has made outstanding contributions to our knowledge of the chemistry of strychnine and brucine, and with Gulland to our knowledge of the chemistry of morphine, codeine and thebaine.

Steroids

Crystallographic studies of sterol derivatives by Bernal in 1932 having shown the inadequacy of the then accepted steroid structure based on the classical work of Windaus and Wieland, led Rosenheim and King to put forward a new formulation for the sterol nucleus which, with but slight modification, has since been abundantly confirmed (154). This vital step was quickly followed by the elucidation of the structural features of the various sterols themselves, as well as of the naturally occurring œstrogens, androgens, bile acids, cardiac glycosides, steroid sapogenins and adrenal steroids. Valuable contributions to the chemistry of the sterols, in particular to cholesterol, ergosterol, zymosterol from yeast and fucosterol from algæ, have been made by Heilbron and Spring. On the synthetic side novel methods for the preparation of polycyclic hydroaromatic compounds, as models for the complete synthesis of a steroid molecule, have been developed by Robinson.

Vitamins

The existence of ‘ accessory food factors ’ (to which the name Vitamin was given by Funk when working at the Lister Institute) was first convincingly demonstrated by Gowland Hopkins in 1912. Heilbron and Drummond were early pioneers in the isolation of vitamin A from fish liver oils, and the discovery of its characteristic light absorption by Heilbron and Morton and the antimony trichloride colour reaction of Carr and Price provide the basis of standard methods of assay. Carr and Jewell were the first to apply the technique of molecular distillation to the purification of vitamin-A concentrates. The work of Heilbron, Drummond and Morton contributed materially to the final elucidation of the structure of this vitamin. Numerous synthetic studies on polyenes related to vitamin A have been made by Heilbron and Jones. The relationship between β-carotene and vitamin A was revealed by Moore in 1930. Heilbron and Morton, in 1938, were also largely responsible for the discovery and isolation of vitamin A_2 from the liver oils of fresh-water fish (146). Peters demonstrated the essential role played by vitamin B_1 in carbohydrate metabolism and the total synthesis of vitamin B_1 was achieved in 1937 by Todd. With Barger three years earlier he had discovered that the vitamin could be oxidised with potassium ferricyanide to give thiochrome, a reaction which forms the basis of one of the most widely used methods of assay. The synthesis of thiochrome by Todd in 1936 established its structure and led to the subsequent total synthesis of the vitamin itself. Todd was also active in the vitamin E field, and synthesised α-tocopherol in 1938, while in the previous year he had isolated β-tocopherol from wheat germ oil as a crystalline allophanate and established its molecular formula (147). The structure of vitamin C (ascorbic acid) was first established by Hirst in 1933 and in the same year its synthesis from l-xylose was announced by Haworth and Hirst (136). The observation that irradiated ergosterol has anti-rachitic properties was made by Rosenheim and King in 1927, in which year Windaus and Hess independently made the same observation, and this led to the isolation of the crystalline vitamin, to which the name calciferol or vitamin D_2 was given (148). The complex stages in the photochemical conversion of ergosterol into vitamin D_2 were elucidated and at the same time the investigations of Heilbron led to the establishment of the structure of both ergosterol and finally to vitamin D_2 as a tricyclic alcohol.

Synthetic drugs and chemotherapeutic agents

In the field of synthetic drugs (167) and chemotherapeutic agents reference must be made to the introduction of acriflavine and proflavine as anti-bacterial agents by Browning in 1917. Mandelic acid as a urinary antiseptic was introduced by Rosenheim in 1935. Sulphapyridine, or M and B 693, the first sulphonamide effective against pneumococcal infections, was prepared by Ewins and Phillips in 1937, and this was followed in 1940 by sulphathiazole or M and B 760, first described by Newbery. Among drugs active against leishmaniasis and trypanosomiasis may be mentioned the glucoside of p-aminophenylstibonic acid of Gray (1924), the amidines of Ewins and the diamino-9-phenyl-10-methylphenanthridinium halides of Walls. The stages which led to the discovery of the remarkable antimalarial properties of paludrine, first described by Curd, Davey and Rose, have revolutionised our knowledge of the relationship between structural factors and antimalarial activity. Mention may also be made of the discovery of the use of 2 : 3-dithiolpropanol, first described in 1945 by Peters, Stocke and Thompson in counteracting the toxic effects of mercury and arsenicals. A preliminary examination of the chemical properties of penicillin was reported by Raistrick in 1932 after the original discovery by Fleming four years earlier (151). Its chemotherapeutic properties having been dramatically revealed by Florey and Chain in 1940 with partly refined preparations in comparatively stable form, fundamental studies into the chemistry of penicillin were carried out by Robinson, Wilson Baker, Chain and Abraham, and by Heilbron and Cook (153), in collaboration with many chemists attached to industrial organisations. As a result of degradation experiments and the synthesis of degradation products, the outlines of penicillin chemistry were revealed in 1942–43 to the extent that synthesis seemed possible. Valuable contributions to the elucidation of the structure of penicillin were also made by means of X-ray crystallography by (Miss) Crowfoot.

EXHIBITS

Organic Chemistry and Biochemistry Panel

128. Silicon compounds. Original specimens of optically active silicon compounds prepared by Kipping.
(Lent by the Science Museum.)

130. Stereochemical models.
(Prepared by Dr. W. H. Mills.)

131. Terpene chemistry. Exhibit illustrating work on the terpenes and triterpenes.
(Arranged by Dr. I. M. Owen from specimens supplied by Dr. J. L. Simonsen, Professor G. A. R. Kon, Professor F. S. Spring, Messrs. Howards & Sons and others.)

133. Alkaloids.
(Exhibit arranged by Dr. H. King from exhibits supplied by the Wellcome Research Institution, the National Institute for Medical Research and others.)

134. Carbohydrates. Original specimens prepared by the St. Andrews School.
(Lent by the University of St. Andrews.)
Specimens to illustrate the work of Harden and Robison.
(Lent by Dr. W. T. J. Morgan.)

136. Carbohydrates and Vitamin C. Original specimens prepared by the Birmingham School.
(Lent by the University of Birmingham.)

137. Viscose: (*a*) specimens of crude viscose film mounted on card; (*b*) film bleached with hypochlorite; (*c*) film dyed with Congo red; (*d*) two letters written by C. F. Cross to Professor J. J. Hummel.
(Lent by the University of Leeds.)

138. Viscose. Bottles used by Cross for making the original preparation
(Lent by the Science Museum.)

139. Viscose. Apparatus of first experimental viscose plant (Topham).
(Lent by the Science Museum.)

140. Thyroxine. Specimens illustrating the first synthesis.
(Prepared by Dr. C. R. Harington.)
Glutathione. Specimens illustrating the first synthesis.
(Prepared by Dr. C. R. Harington.)

144. Collection of specimens prepared by Thudichum.
(Lent by the National Institute for Medical Research.)

145. Oils and fats. Specimens illustrating work on the constitution of natural oils and fats.
(Prepared by Professor T. P. Hilditch.)

146. Vitamin A.
(Arranged by the Imperial College of Science and Technology.)

147. Vitamins B_1 and E.
(Prepared by Professor A. R. Todd.)

148. Vitamin D. Original apparatus in which vitamin D was first prepared together with original specimens.
(Arranged by Dr. H. King.)

149. Sex hormones.
(Arranged by Professor G. F. Marrian.)

150. Hormones—Synthetic œstrogens, etc.
(Arranged by Professor E. C. Dodds.)

151. Mould metabolic products.
(Prepared by Professor H. Raistrick.)

153. Penicillin. Specimens illustrating work on degradation and synthesis.
(Lent by Sir Ian Heilbron.)

154. Steroids.
(Arranged by Dr. H. King from specimens supplied by various sources.)

155. Accum's coal tar products.
(Lent by the Museum of the History of Science, Oxford.)

156. Benzene (Faraday's original samples).
(Lent by the Science Museum.)

157. Bramah press (Faraday). Small press used to dry frozen benzene.
(Lent by the Royal Institution.)

158. Coal tar constituents. Collection of pure constituents and derivatives.
(Prepared by the Chemical Research Laboratory, Teddington.)

159. Hydrocarbon derivatives. Collection of specimens. Illustrating the work of Armstrong and Wynne.
(Lent by Imperial Chemical Industries Ltd.)

160. Fluorescence of hydrocarbons. Demonstration of fluorescence and separation of hydrocarbons by chromatography.
(Prepared by the Imperial College of Science and Technology.)

161. Solid paraffin. Original sample first prepared by John Thom in 1836.
(Lent by Professor Cumming.)

162. Relics of W. H. Perkin. Collection prepared from exhibits in the possession of Miss A. F. Perkin, the Science Museum, the University of Leeds, Mrs. A. G. Perkin, and others.
(Arranged by the Science Museum.)

163. Meldola. Collection of original specimens.
(Lent by the Chemical Research Laboratory.)

164. Hofmann. Samples of Rosaniline dyes prepared between 1858–63.
(Lent by the Science Museum and Imperial College of Science and Technology.)

165. Phthalocyanine. Collection of pigments.
(Lent by the Chemical Research Laboratory.)

166. British developments in the dyestuffs industry. A comprehensive exhibit.
(Prepared by Imperial Chemical Industries Ltd.)

167. Synthetic drugs.
(Arranged by Dr. H. King from exhibits derived from various sources.)

168. Synthetic rubber. Specimen of synthetic rubber prepared by Tilden from isoprene.
(Lent by the Science Museum and the University of Birmingham.)

169. Synthetic rubber. Exhibit showing later work of Matthews.
(Lent by Dr. W. J. S. Naunton.)

170. Celluloid (Parkesine). Exhibit of original specimens and photographs, showing the early work of Parkes.
(Lent by the Science Museum.)

CHAPTER X

ANALYTICAL CHEMISTRY

Stoichiometry

THE most fundamental analytical work is the determination of atomic weights. Among British contributors in this field Thorpe, Baker and Briscoe may be mentioned (p. 38).

In the application of precision gas-density measurements to stoichiometric problems Rayleigh's work on hydrogen and oxygen was outstanding. The determination of the atomic weights of nitrogen by Whytlaw-Gray (1905) and of chlorine by Whytlaw-Gray and Burt (1909) were made by gas-density methods (p. 38). The former of these was particularly notable in that gravimetric and gas-density methods, which had up to that time given conflicting results for nitrogen, were both used and shown to give consistent values. More recently workers of Whytlaw-Gray's school have redetermined the atomic weights of carbon, nitrogen and fluorine by the gas-density method using the improved form of quartz microbalance (Cawood and Patterson, 1936).

Mention should also be made here of the evaluation of many atomic weights by Aston's mass spectrographic method (p. 33).

Gas analysis

The foundations of gas analysis were laid by Cavendish and Priestley during their investigations upon the atmosphere in the years 1783–85. Methods of manipulation were developed by Priestley, including the use of mercury as a confining liquid and the construction of the eudiometer. The principle of the measurement of the contraction in volume of a gaseous mixture after removal by successive chemical reactions of the various constituents, first worked out by Cavendish, was elaborated by subsequent chemists including Davy and Faraday (171).

Methods of air analysis were revolutionised by the work of J. S. Haldane, whose well-known apparatus was first described in 1898 (172).

An important new principle was introduced in the Bone-Wheeler apparatus, described in 1908, which made use of the measurement of pressure at constant volume instead of volume at constant pressure. The Bone-Newitt apparatus (172) described in 1930 by Bone, Newitt and Townend, is a high-precision instrument of the Bone-Wheeler type.

Water analysis

Water analysis and its application to the control of public water supplies were early developed in Great Britain and it may fairly be claimed that we led the way in this important field.

The early attempts at water analysis were mainly concerned with the mineral constituents and Boyle may be said to be the pioneer. More elaborate methods were later devised and by about 1800 very complete analyses showing the amounts of dissolved gases and mineral constituents were being published.

The sanitary aspect of water supplies had not received much attention at this time, but in 1841 Dr. T. Clark published his water-softening process in which the Soap Test which bears his name was described. In the *Lancet* in 1850 Dr. A. H. Hassall called attention to the importance of micro-organisms in drinking water and made micro-examinations of the London supplies. Soon after, the Board of Health appointed three Commissioners—Graham, Miller and Hofmann—to investigate the Metropolitan water supply. In 1856 Hofmann, in a report to the Board, drew attention to defects in the methods of analysis in use, and by 1865 monthly analyses of the London supplies were being made by Hofmann, and Miller published an important paper on the subject in our *Journal*. Edward Frankland succeeded Hofmann, and in 1868 elaborated, in conjunction with H. E. Armstrong, the combustion process for carbon and nitrogen which bears their names; and in the same year Wanklyn and Chapman published their important process for the determination of ' albuminoid ' ammonia. Chemical methods were now assuming the form which is familiar to analysts of the present day. Frankland by his work on the various Royal Commissions, succeeded in making London's water supplies the most carefully controlled in the world.

In 1871 Burdon Sanderson again directed attention to the presence of bacteria in water, and in 1885 Percy F. Frankland published his gelatine process of water-examination for London waters, and his book *Micro-organisms in Water* (1894) deals with the sanitary aspects of water supply.

While recent work, by Sir Alexander Houston and others, has emphasised the need for systematic bacteriological examinations before an opinion on potability can be given, the chemical examination is still of fundamental importance especially where decisions are required as to the dangers that a water may cause corrosion or tend to dissolve lead or other poisonous metal. Furthermore, attention has been focused on the treatment of water for boiler purposes, and for other industrial requirements.

Chemical methods of analysis of waters have adapted themselves to modern needs and developments include the use of tintometers and coloured glass discs in routine methods (173).

Marsh's test

Marsh's test for arsenic was first described in the *Edinburgh New Philosophical Journal* in 1836. The hydrogen evolved from pure zinc and dilute sulphuric acid containing the material to be examined. If the material contained arsenic, a piece of glass depressed on to the gas flame condensed a ' mirror ' of arsenic (174). The test with small improvements remained in this form for many years.

In 1891 Sanger described the adaption as a quantitative test by the use of standard mirrors. In 1902, at the time of the epidemic of poisoning by arsenic in beer, a joint committee of the Society of Chemical Industry and the Society of Public Analysts standardised the test.

The electrolytic modification seems to have first been suggested by Bloxam in 1861, and in 1903 a committee under the Chairmanship of T. E. Thorpe reported to the Royal Commission on Arsenical Poisoning, recommending a carefully designed apparatus with electrodes of platinum, and a standardised technique (174). Later, in 1927, Aumonier described an improved apparatus in which mercury, the metal best suited to give constancy of surface and high cathodic overvoltage, is substituted for platinum, together with other improvements. This apparatus is at present in use at the Government Laboratory (174).

Hydrometers

The use of hydrometers for the rapid determination of the density of liquids has long been the general practice in laboratory work, but the hydrometer was in fact originally evolved in Britain to meet the need for a rapid determination of the composition of alcohol-water mixtures in connection with the duties which have been levied on spirits since the sixteenth century. It was Robert Boyle who, in 1675, first demonstrated the use for such purposes of a glass float weighted with water or mercury.

The instrument now used officially by revenue officers is the hydrometer of Bartholomew Sikes, legalised for this purpose in 1816 (175). This hydrometer is of metal, similar to that designed by Clarke in 1725, and it is made applicable to a series of ranges by the attachment of successive weights. The necessary measurements of specific gravities of alcohol-water mixtures at various temperatures were made with remarkable accuracy under the auspices of the Royal Society by Blagden and Gilpin in 1790–94. The readings of this instrument are on an arbitrary scale and reference tables (which were revised at the Government Laboratory in the years before 1916) give the alcoholic strengths in terms of ' proof spirit.'

Another hydrometer, that of Bate (1823), is also in standard use for revenue purposes to determine the specific gravity of liquids used in brewing (175). This instrument is graduated to read true specific gravities.

pH Indicators

The conception of pH and the use of pH indicators was mainly developed by workers on the Continent and in America. Among British workers in this field are Tizard, Prideaux and Britton.

The convenient method of pH determination by comparison with standards in capillary tubes filled with buffer solutions and the indicator was developed from a suggestion by Mr. H. A. Ellis (176). The idea of the Universal Indicator showing the colours of the spectrum in correct order as the range of pH is traversed was suggested by Dr. J. Moir (1917), and various mixtures of indicators may be used for this purpose (176). His original mixture contained methyl red, α-naphthol phthalein and phenolphthalein.

Colorimetry

Lovibond's method of colorimetry permits of the measurement and standardisation of the colours of liquids and has found very wide application.

It originated in 1884 in an instrument for measuring and recording the colour of malt worts, beer and similar liquids, with the aid of a series of standard glass slides (177). It was subsequently extended so as to be applicable to the measurement of the colour of any liquid. The method was developed empirically, but in a scientific manner. It may be applied to the determination of small quantities of ammonia, chlorine, iron, lead, copper, nitrates and nitrites in water, for pH measurements and many other purposes.

SPECTROGRAPHIC ANALYSIS

The earliest applications of spectroscopy to analysis were of a qualitative character, and the first suggestion of methods which might give quantitative data was made by Lockyer about 1873. The main impetus to the development of semi-quantitative methods came from W. N. Hartley, who by 1884 had drawn up his tables of persistent lines given by solutions of salts fed to a spark discharge. This work was continued by Pollok, and these workers, together with de Gramont in France, had by 1920 laid the foundations on which modern quantitative spectrographic analysis is built.

One essential for such development was a suitable spectrograph, and the Hilger Quartz Spectrographs were designed by Twyman (1909–11). These instruments, or copies of them by other manufacturers, have been responsible for most of the quantitative spectrographic analysis which has been carried out.

Amongst those whose work pointed out the possibilities of spectrographic methods were Judd Lewis and Ramage, the latter of whom illustrated with his flame technique (1929) the many applications possible in biological investigations. The first industry to explore fully the benefits of the method was the metal industry, led by D. M. Smith, working with non-ferrous metals, whilst in recent years has been seen the widespread adoption of flame, arc and spark methods in metallurgy, agriculture, geology, medicine and general chemistry, yielding quantitative results with an accuracy of between ± 2 per cent. and ± 10 per cent. in most instances (178).

Ultra-violet absorption spectra

Hartley and the early workers recorded the absorption spectra of organic compounds qualitatively and found many instances of differences between isomerides striking enough to decide the structures of related substances for which there were alternative formulations.

The advent of photographic spectrophotometry permitted the accumulation of a vast body of fairly quantitative data on pure substances both inorganic and organic. During the period 1910–30 the data were reduced to order and the interpretation of solution-spectra made progress, on semi-empirical lines, great enough to raise spectrophotometry to the level of an almost indispensable tool in the study of many constitutional problems.

Parallel progress in the interpretation of the spectra of vapours narrowed the gap between the theory of spectra of polyatomic and diatomic molecules. From 1925 onwards solution spectra played a considerable part in advancing biochemistry.

The contribution made by the scientific instrument maker has been important throughout and has reached a new stage with the production of easily operated photoelectric spectrophotometers, permitting the attainment of sufficient accuracy to make the method a precise analytical aid.

Infra-red spectra

Although the discovery of infra-red radiation was made by Herschel in England in 1800, the spectroscopy of that region was virtually ignored by British workers for over a century. Shortly after the last war work was initiated by Robertson and Fox at the Government Laboratory, by Rideal, Rawlins, Snow and Taylor at Cambridge, and by Bailey at University College. These workers examined the spectra of many simple polyatomic molecules, establishing their configuration and determining many of their structural constants (*e.g.* fundamental frequencies, inter-nuclear distances and force constants) with great accuracy. The work at Cambridge was subsequently developed by Sutherland, who introduced techniques of higher resolving power and observation at liquid air temperatures. Shortly before the war Thompson took up the study at Oxford, and during and since the war these last two workers have done much to increase the speed and accuracy with which spectra can be recorded, over the range 2–15μ, in which occur the majority of the absorption bands which characterise a chemical compound. A pen and ink record of this region can now be obtained in a time of the order of fifteen minutes, while smaller sections within this region (2–4μ in extension) can be displayed on a cathode ray oscilloscope under only slightly lower resolving power (178). This enables one to make identifications of compounds in a time of the order of fifteen seconds and also to follow changes in spectra arising from chemical reactions or, for example, in the course of purification by distillation. Double beam spectrometers have been developed which automatically cancel out the effects due to atmospheric absorption, especially troublesome in the region 5–8μ. One great advantage of the infra-red method of analysis is the small amount of material required. In general 0·05 gm. is sufficient, but in certain cases identifications have been done on amounts of the order of a milligram. The infra-red absorption spectrum of a chemical compound may well be regarded as its most distinctive physical property, the nearest approach so far achieved to a ' chemical finger print.' As a result it has been possible to apply the infra-red method of analysis to a very wide range of chemical problems, *e.g.* petroleum, plastics, rubber, coal tar derivatives, amino-acids and penicillin. Examples have been chosen to illustrate the application of the infra-red method to problems in various branches of chemistry.

EXHIBITS

Analytical Methods

172. Gas analysis, illustrated by Frankland's apparatus, Haldane's apparatus and the Bone-Newitt apparatus.

173. Water analysis, illustrated by the B. D. H. Lovibond nessleriser and a portable case for water and food analysis on active service.

174. Marsh's test, illustrated by a model of the original Marsh apparatus, electrolytic apparatus with platinum electrodes and a modern apparatus with mercury electrodes.

175. Hydrometry, illustrated by specimens of Sikes' hydrometer, Bate's hydrometer and others.

176. pH indicators, illustrated by the B. D. H. capillator and universal indicators.

177. Colorimetry. The original tintometer and a modern tintometer. (Lent by the Tintometer Co.)

178. Spectrographic records illustrating the analytical applications of spectrography.

The Exhibits in this section were arranged by Dr. G. M. Bennett and supplied by the Government Laboratory, the Science Museum, Mr. G. H. Gabb, Messrs. Baird and Tatlock, the British Drug Houses Ltd., the Tintometer Ltd., the Cambridge Instrument Co. Ltd. and others.

INDUSTRIAL CHEMISTRY

As an addition to the Centenary Exhibition, arrangements have been made with the Science Museum to reopen its collection of industrial chemical models and appliances. This collection, which will be on view in gallery 66, is mainly historical, but some good models of recent plant are included and will be augmented as opportunity allows. Among other subjects, the collection illustrates the early history and development of the acid and alkali, the mineral oil and the coal-tar industries. Fermentation processes are well represented and models of explosives plant are included.

Section 2

CHEMISTRY IN EVERYDAY LIFE

by DR. JAMES LAWRIE

THE extent to which everyday matters, the common domestic and personal operations, are now dependent upon chemistry is not fully appreciated—largely through familiarity ; for what are such culinary adjuncts as baking-powder, salt, washing soda, soap substitutes, etc., but chemicals so necessary and so familiar to modern life that they are regarded almost as natural products.

Every time we take an aspirin, mix cement for the garden path, paint the front door or write a letter, we are using the products of applied chemistry, just as when the housewife buys a loaf of bread, she purchases one of the most complicated chemical reactions known.

This part of the exhibition is designed to give a clearer idea of the ramifications and importance of chemistry in everyday life and, by detailing a few only of the myriad possible items, endeavours to show how the chemist works and the actual operations he puts into practice to secure the desired result, which may be needed for medicine, industry, agriculture or the home.

A salient fact emerges almost at once. It is that the chemist is part of a team, a team based upon the labours of coal-miners, farm-workers, fishermen, engineers, industrialists, retailers and consumers. The part played by each is indispensable, not the least important being the actual consumer or user, for if the final product is misused the efforts of all are negated. If the products are wisely and correctly used the labours of all are crowned with completeness.

Raw materials for the chemist to treat and from which to secure natural products, or which to alter and adapt in construction so that virtually new and useful products are formed may, for the sake of simplicity, be divided into two classes—Capital resources, which are limited because world supplies are limited, and Income resources, which are cyclical and renew themselves by natural processes.

INORGANIC MATERIALS—CAPITAL

Since the world began deposits of coal, salts, oils and minerals have been accumulated to become, at varying stages of our civilisation, raw materials which the chemist uses for essential manufactures. Supplies of these basic materials are limited—sooner or later, for example, the world will run short of coal and oil—but this inevitable ending will not necessarily worry mankind at the time of its happening since science, and chemistry in particular, has already done much to provide alternative materials, and will do more, to replace those products of which our limited natural supplies are steadily dwindling.

From the capital stocks in the earth we derive the minerals and ores from which, by chemical operations, are obtained the metals needed for industry. Thus iron is smelted from hæmatite, copper from malachite and aluminium from bauxite. The actual metal may be only a small fraction of the ore mined and, in some cases, literally tons of ore may be needed to produce ounces of metal.

Sands, which may be of a complex nature, enable us to make glass. Pottery is made from clays, and mixtures of sand, coke, clay and anhydrite provide cement, together with the chemicals sulphuric acid and sulphur dioxide.

Coal, so aptly described as the source of the vital flame, provides us with heat and power for factories, transport and the home. When carbonised it gives us gas, tar, and coke which is used in organic chemical and metallurgical processes. By distilling the tar the chemist obtains ammoniacal liquors, road tars and oils, from which he makes benzene, toluene, phenols, disinfectants and chemical bases from which are made thousands of chemicals and a vast range of dyes.

Oils, salt, phosphate and many other substances similarly provide the chemist with a starting material for his operations in this field of limited supplies.

ORGANIC MATERIALS—INCOME

Naturally and constantly occurring supplies come to us from plants, animals, water and the air—supplies which, reproducible, are practically unlimited as is evidenced by the nitrogen cycle in which nitrogen passes from the soil to the plant, from plant to animal and back, as manure, to the soil. With this is linked the carbon-oxygen cycle which, via green leaves and plants, goes to animals and, by combustion, breathing and decay, back to the atmosphere.

Crops are mainly grown as foodstuffs, but the chemist uses them also to make important industrial requirements by converting grain, starch and sugar by fermentation into ethyl alcohol, which in turn he converts into essential materials such as acetone, acetaldehyde and acetic acid. Even the plant fibres are used to make paper and other cellulose products.

Air is a mixture of nitrogen, oxygen, rare gases and carbon dioxide. Apart from the natural processes of breathing and decaying by animals and plants, the air provides us with its component gases, obtained by separation. Medicine and industry use oxygen for resuscitation and welding, etc., nitrogen is used to make fertilisers and explosives, whilst the rare gases argon and neon find use in lighting equipment.

Seas, rivers and rain are an inexhaustible supply of water, which is a mixture of hydrogen and oxygen gases. The chemist can separate these and obtain them in a pure state. Water itself can be used as a source of power or be converted to steam, thus converting heat into power. Sea-water, which covers nearly three-quarters of the earth, contains salt, magnesium and bromine, all of which are extracted on the commercial scale for industrial use.

From the foregoing it will be seen that our resources are many and that the ingenuity of scientists is fully capable of extending our control and use of the materials we possess and that new, man-made, products can be manufactured from natural bases.

OPERATIONS AND PROCESSES

To utilise natural supplies to the best advantage has called for the development of many involved operations and processes of which grinding, mixing, heating, and the application of pressure are the most obvious. Whenever possible the chemist makes use of natural physical changes, the simplest being that of water, which can exist as solid ice, as a liquid and as a vapour.

Intimate contact is needed for chemical reactions, and solids may be ground, mixed, melted or dissolved in liquids. Gases mix easily but sometimes need high pressures. They can be made to contact spread-out solids and can be bubbled through liquids.

Contact between substances may itself bring about reaction and often this reaction produces so much heat that cooling devices, using water, ice or solid carbon dioxide are needed.

Separation is another step in manufacture. Solid products can be filtered off or separated in a centrifuge. Gases can be collected, liquefied or stored under compression in cylinders. Extraction with solvents, adsorption methods and fractional distillation are also used.

When separated, some purification of the product is usually necessary, and in some cases this may be easily done by washing with water or other solvent. Alkalis and acids may be needed for this purpose, and crystalline solids are purified by repeated recrystallisation. The vacuum or molecular still may be used for materials sensitive to temperature changes.

Of the many processes used by the chemist and applied in his treatment of raw materials, we may cite a few of the more important, such as splitting and addition. A compound treated with acids or alkalis may be split into several products, water elements being added. This is known as Hydrolysis and is used, for example, when cane sugar, digested with dilute acid, yields glucose and fructose. Fat, digested with an alkali, undergoes what is known as Saponification and yields glycerol and sodium stearate. If the chemist unites a substance with itself and at the same time eliminates water or other matter, this is known as Condensation, a process operated when small units of a substance are repeatedly condensed to form Nylon fibres.

The repeated process of adding one compound to itself or to another compound, but *not* eliminating water, is called Polymerisation when only one type of molecule is involved. This is a basic process for making synthetic high polymers so that if ethylene is added to ethylene and so on, the industrially valuable compound polyethylene results.

If more than one kind of molecule is used the process is called Copolymerisation, as when butadiene added to styrene yields synthetic rubber.

This very brief and necessarily incomplete review of the operations and processes used by the chemist will enable us to follow those applications which bring materials into use or subject them to treatment. Refined copper, for example, can be used by itself or as a component of an alloy. Plastics can be prepared and machined and moulded without further chemical treatment.

The use of the processes mentioned is exemplified in the preparation of Vitamin A from fish liver oil, a process using nitrogen gas to prevent oxidation of the product, the gas first being purified by passing it through chemical solutions to remove traces of oxygen and sulphur. The fish liver oil is digested with an alkali (Saponification), the unsaponified portion being that which contains the vitamin, mixed with cholesterol. This cholesterol-vitamin portion is shaken with ether, which dissolves it and the two portions are separated (Extraction). Washing with water follows to remove all alkali, and traces of water are removed by means of an anhydrous chemical (Washing and Drying).

The ether is removed by heating, the vapour being cooled, condensed and collected for further use (Distillation). Nitrogen gas, bubbling through the contents of the still, removes the final traces of ether, leaving the vitamin-containing substance in the flask. This mixture is dissolved in methyl alcohol and frozen, which causes the cholesterol to crystallise out (Crystallisation), leaving the vitamin in solution.

The methyl alcohol is distilled off under vacuum and recovered for further use, leaving the vitamin in the original non-saponifiable matter from which it is separated by further distillation in the molecular still in which, diluted with vegetable oil, the material is passed over a distilling surface at about 120° C. About 2 cm. distant from this surface is a cool, condensing surface, the space between being highly evacuated. The purified vitamin A collects on this cold surface and the process is at an end.

The manufacture or preparation of vitamin A is an excellent example of the manner in which the chemist uses chemical and physical processes to obtain materials which are vitally important to humanity. In many cases the process does not end with the preparation of a pure, natural product. Sustained research has enabled chemists to prepare synthetic products which are chemically identical with the natural products or which contain, at least, the active ingredient of that product, and it is often possible, with drugs, for example, so to alter their chemical construction that, whilst the active principle is retained, non-effective or possibly harmful ingredients are altered to become effective or harmless.

With this very brief introduction to the way in which the chemist works, we may proceed to a discussion of the exhibits shown, bearing in mind that, it being possible to display only a few examples, these must be taken as representative items illustrating how the chemist and his work enter into every phase of modern life. The matters discussed have been selected because they impinge upon the lives of us all and at the same time show how important, as well as interesting, is the work of the chemist—it is probably correct to say that in almost every material or product we use for any purpose the chemist plays *some* part in its production and development. Let us take five broad divisions of human activity and needs.

AGRICULTURE AND FOOD

It is not possible for man to feed himself on simple chemical substances—he requires his food in the complex forms made by plants and animals, so that substances taken from the soil by plants which are eaten by animals, ultimately find their way to the human system. With cereals, pulses and fruits the same process occurs and mankind's primary activity becomes that of ensuring the existence of sufficient crops and animals for his needs. Scientists have not yet learnt how to do what the plant does, but they are learning how it is done—the investigation calling for a high degree of technical ability and knowledge, coupled with infinite patience.

As his target, the agricultural chemist has the maximum increase possible in the yields of crops. This he does by feeding plants and protecting them from insect and other enemies. Feeding plants is effected by the use of fertilisers—practical study of various crops under controlled conditions enabling us to know the amounts needed by the plant in question. Major nutrients, such as nitrogen, phosphorus and potassium, are obtained by plants from the ground and these foods need replacing as the soil becomes exhausted.

Natural nitrates for this replacement had to be mined and shipped to this country, and natural nitrates are part of our capital of limited supply. The chemist has overcome any fear of nitrogen scarcity by his ability to separate nitrogen from the air, of which the gas forms four-fifths, and by making it combine with hydrogen, to form ammonia, which is easily transformed into fertilisers thus providing the farmer with an unlimited supply of nitrogen—what was part of our capital stock now becomes income and nitrogenous fertilisers can be manufactured here in Great Britain.

The use of fertilisers is not, however, so simple as the bald statement of nutrient replacement would indicate, the soil itself serving only to hold nutrient foods and provide support to the plant. Plants can be grown in water if the right foods are added in correct amounts ; this is the science of hydroponics. Correctly applied fertilisers produce great increases in crops, but factors such as the heaviness of the soil, its acidity, etc., materially affect the availability of the fertiliser to the plant. For proper use fertilisers need a combination of practical experience and scientific knowledge such as the farmer and the Ministry of Agriculture's advisers provide—a service of which farmers wisely make increasing use—and the amounts of fertilisers used have increased rapidly, but they are not yet used as freely as they could and should be.

In addition to major nutrients there are a host of other elements—trace elements—which the plant requires in much smaller quantities. Without these trace elements plants suffer characteristic defects which can be recognised, or they exhibit deficiencies which can be checked by chemical analysis. Defects in the supply of trace elements can be corrected by spraying the missing substances over crops or, in some cases, by injecting them into the plant itself. Too much of these elements leads to poisoning of the plant, for example, manganese must be present to the extent of at least 10 parts per million, but more than 100 parts per million will poison the plant. If soil conditions are not quite suitable, *i.e.*, incorrect acidity, what was an excess of manganese may become a deficiency.

It is obvious that only little of the plant foods in the soil are available to the plant, and as has been indicated, factors such as heaviness of the soil affect the availability of fertilisers. Sugar beet, for example, can be made to yield bigger crops by adding potash or phosphate to the soil, but the yield depends upon the solubility of the fertiliser. This means that it is not possible simply to find out what foods a plant needs and then analyse the soil and add what is missing. It is much more complex than that, and calls for great practical experience as well as for scientific knowledge. A soil may become dangerously acid in wet regions where calcium is washed out of the ground, and for correcting this lime must be added. An instrument has been devised which tests the acidity of soils, enabling the need for lime to be judged.

Chemists and botanists have joined with farmers in the never-ending battle against the plants' enemies, such as insects, fungi and other plants. Great developments are taking place in the devising of weed-killers, and new chemicals are available which have selective effects upon plants and which can be used to kill weeds without harming crops, thus saving labour previously used in uprooting weeds, which compete with the wanted crops for light, air and food.

The importance of weed removal and prevention is shown by the fact that the fast-growing Yellow Charlock (*Sinapis Arrensis*) can entirely choke a field of onions so that no crop is obtained at all. In cereals up to 200 per cent. increase follows its removal.

Poisonous chemicals such as sulphuric acid, sprayed at 94 lbs. to the acre, or copper chloride at 10 lbs. to the acre, are effective against some weeds. Recent discoveries have evolved substances which promote the growth of some plants, for example, 2 methyl-4-chlorophenoxyacetic acid, called 'MPCA' and 2-4 dichloro-phenoxyacetic acid, called 'DCPA'; but these will kill plants if given in too great a quantity. They only affect certain plants, so they can be used to kill these plants growing among crops, which are themselves unaffected by these chemicals. These new weed-killers are used in much smaller quantities—about 1 lb. per acre, and there is now a choice of selective weed-killers for different crops.

Similarly, dusting powders and sprays are effective against such insect enemies to plants as the Colorado beetle, apple bugs, beet beetles, caterpillars, weevils, aphis and onion flies, etc.—there are far too many to list. Chemicals such as D.D.T. and Gammexane and related chemicals, are now increasingly and successfully used.

Diseases and fungi are other and costly problems to the farmer—particularly fungus diseases of cereals, which account for untold losses, literally thousands of bushels of cereals are spoiled every year. The control of the disease, known as 'Covered Smut,' can be taken as an example of the chemists' aid to the farmer in this particular battle.

During threshing the infected grains are broken up and spores from them are blown about to settle on and to infect healthy grain. The chemists' remedy is to mix the seed with a fungicidal powder which contains certain organo-mercury compounds that kill the smut spores on the surface of the grain. Much seed is now sold already dusted with these powders, but farmers can easily do this themselves by mixing a little of the powder with the grain.

The main ingredients of these new seed dusting powders are carriers such as talc mixed with an organo-mercury compound such as phenyl or ethyl mercury acetate, chloride or phosphate. In some powders the amount of chemical may be only 1 to 2 per cent. The introduction of organo-mercury seed dressings is a chemical advance of great value and a milestone on the road to the conquest of seed-borne diseases.

In all these matters it must be remembered that the extra crops which can thus be produced and made into food are only of value if good use is made of that food. Chemical study of nutrition and food factors has helped greatly in this. To the housewife food consists of so much meat, vegetables, bread and other purchases to be made at the shops. But by studying its chemical nature and its effect upon the body, the chemist regards food as made up of so many chemical factors such as protein, vitamin, carbohydrate and mineral salts. By finding out the body's requirements of these factors in different conditions and the proportion of them contained in different foods, it is possible to ensure that an adequate and well-balanced diet is provided for adults or children. Chemistry plays an important part in this proper utilisation of food.

It will be useful here to touch upon one of the oldest of natural foods, wheat, and upon a relative newcomer—margarine, a product of chemical technology.

Despite man's ancient usage and experience of wheat, it is obvious to moderns that care must be taken that, in cooking or processing, nothing is destroyed or lost of the nutritionally valuable constituents contained in the wheat. This has involved scientific study from the early seed stages to the finished production of a loaf of bread.

It is not possible to make good bread from any kind of wheat—each variety has its subtleties which, so far, have defied elucidation by the chemist, and it is not yet possible to tell, by chemical analysis, whether a wheat will be good for bread-making. To make bread as we like it in this country, flour is made from a blend of English grain and imported grain. Technical control commences, of course, with fertilisers in the field. Our grain is moist, containing up to 22 per cent. moisture when cut, and this total is reduced in the traditional way by stooking in the sun and air to reduce the moisture content to below 15 per cent., which is the safe limit for storing. If wet weather persists, or if grain is harvested by simultaneous cutting and threshing, then it must be dried by heating before it is stored.

Great care must be taken when grain is heated. Over-heating will kill the grain (for even when cut it is alive and breathing), and it is then only with difficulty used by the miller, and is useless for malting and for seed. It is difficult to lay down hard and fast rules for drying, but possible damage to dried wheat can be detected by examination of the enzymes present and it is probable that chemical tests will be devised for rapid estimations of any damage. Such tests involve a study of the denaturing of the protein of the grain, and it has been discovered that there is a most striking parallel between the damage to grain by heating and the damage to animal tissue by burning.

This is an excellent example of the indivisibility of science. Medical research workers on burn treatment have had difficulty in obtaining ' standard ' burns, but the use of grain protein enables a degree of such standardisation to be obtained and medical and grain research workers have been able to give each other help in these two apparently dissociated fields of enquiry. It might be as well to mention that this substitution of another substance for that upon which the research is directed is quite a common occurrence. Rubber, for example, is a complex system of molecules and, for convenience and simplicity, much research on rubber is actually carried out with the molecules of olefines such as squalene—the results can be applied to rubber.

To return to wheat. It was necessary to discover how the nutritionally valuable constituents of the grain are distributed throughout its bulk. This is done by dissecting single grains and analysing very small quantities of the different parts. This analysis established that most of the vitamin B_1 is contained in the scutellum, which is a very small part at the germ end of the grain. It is now possible to estimate the vitamin B_1 by fluorescence in ultra-violet light, a delicate test by which very minute amounts can be assessed. This means that these portions of the grain should be present in the flour and that the hard outer layer be rejected. This is achieved in the National flour now in general use, a result obtained by the close working collaboration of chemist and milling engineer.

Chemical control does not stop at ensuring that the nutritive parts of wheat grains are conserved during milling. The chemistry of bread-making has extended to the bakehouse and a great deal has been discovered about this most complex process, so that bread-making has been improved and has become more reliable. Such scientific knowledge has made it possible to overcome any national deficiency of necessary factors as the vitamins, or even of such homely chemicals as calcium—both of which have been added to our bread in recent years.

Bread has a habit of becoming stale and unappetising, a fact which results in considerable waste. Much work has been carried out by chemists to discover some additive which would at least retard this process. Some success has attended this research and the bread supplied for the invading forces in Normandy was so treated that staling was delayed for a period, thus ensuring palatable bread for our warriors until such time as field kitchens could be assembled. This, however, was only a partial success, and it is clear that complete success in the search for an anti-staling medium would be significant, and would mark a turning-point in the feeding of smitten Europe.

The study and application of chemistry must extend beyond such problems to include consideration of new processes and to ensure that these do not destroy nutritive qualities in foods and, what is also of importance, that the appearance remains attractive. This last factor is seen as a major item when we give attention to the preparation and food properties of Margarine, a compound taking the place of butter.

Margarine is now a very different substance from the very suspect, insipid material of its early days. It is made, as the exhibition has shown, from the oils or fats obtained from peanuts (ground nuts), dried coconut (copra), palm kernels, cotton seed and soya bean by extraction or crushing and from whale oil. After a process of refining, which removes free fatty acids, the oils are bleached and deodorised. In the case of whale oil, which is an important raw material, the hardening process of hydrogenation is used. This alters the oil to a solid fat and at the same time removes any fishy odour or taste. This chemical process is of the greatest importance, as it enables us to use a fat prepared from raw materials which would otherwise be unsuitable for margarine making.

Liquid vegetable oils are often similarly treated to give solid fats, the hydrogenation process being that of saturating the double bonds of the molecules by passing hydrogen through the oil under pressure, a nickel catalyst being used to further the reaction. By controlling the conditions of hydrogenation it is possible to produce a product of any desired consistency.

Refined, hardened oils and refined unhardened oils are then mixed in mechanical churns with vitamins A and D. Vitamin A is prepared from fish liver oil, as has been described, whilst vitamin D is prepared by irradiation with ultra-violet light of the substance ergosterol, which is obtained from yeast. Any trace of rancidity in the fats would destroy the vitamin A and the chemist is at great pains to prevent this destruction. At present 550 units of vitamin A and 90 units of vitamin D are added to each ounce of margarine.

The story does not end here. Margarine, like butter, is an emulsion of water in fat. Emulsifying agents, such as the partial esters of glycerol, are added to assist in maintaining the water in a state of fine dispersion throughout the mass. To increase nutritive value milk is added to the margarine and the milk itself is subjected to a special bacterial ripening treatment which develops a desired flavour.

One of the chief flavouring constituents of butter is the substance diacetyl, and this is added to margarine to produce a butter-like flavour. Salt is usually added to give flavour and improve the keeping qualities.

Margarine is thus produced by chemical processes and subject to strict chemical control, as a palatable and nutritious foodstuff containing those accessory food factors such as vitamins which are so necessary to the maintenance of health. More and more is mankind relying upon chemistry in his search for defence against ill-health, and more and more is chemistry providing him with the answer.

HEALTH

We have seen how interlocked are most problems of food and health and how, in research on wheat, medical research on burns has been advanced. Man has used chemistry with good effect in his never-ending battle against those micro-organisms which cause disease. Destruction of these germs can be effected in the body by the use of drugs, or outside the body by controlling their insect or animal carriers. Close collaboration between chemist and doctor has led to magnificent advances of this kind, and such compounds as D.D.T. and Penicillin inevitably, and properly, come to mind representing, as they do, profound and far-reaching weapons in medical science and hygiene. So vast is this field that it is possible only to discuss one such subject, that of malaria. It is no exaggeration to say that the complete eradication of malaria from the world becomes possible by means of widely and wisely used medical and scientific collaboration.

Let us first realise the seriousness of this problem. It is estimated that three million people die every year from malaria, and that this number can be multiplied by ten to account for indirect deaths caused by diseases for which malaria has opened the path. Of the population of the world, 1 in 7 suffer from malaria, and the cost to humanity in suffering cannot be expressed in pounds sterling, although it is apparent that the wastage of man hours through illness on this score alone is an economic problem of gravity.

It must not be thought that malaria is a disease confined to torrid and tropical zones, or to those humans who have been infected in those zones. Carried by mosquitoes, the germ travels wherever the mosquito wanders, and the advent of rapid air transport tends to increase the dispersion of these insects, despite the hygienic precautions taken of spraying aircraft, etc. Holland, during the war, suffered badly from malarial epidemics, and Great Britain has danger patches which scientific survey has mapped as being likely foci of the disease, or are already such.

Malaria has for long been treated with quinine, but the war-time cessation of supplies led to an intensive search for new drugs. A brilliant research based on chemical and medical studies resulted in the development of Paludrin, which has proved to be the most effective anti-malarial yet prepared. In addition, it is cheap to make and safe to use. Chemistry has by this discovery released mankind from dependence on naturally-produced quinine in the fight against this disease, and collaboration between chemist and doctor will undoubtedly yet further improve this drug.

Malaria is also attacked by fighting the mosquito which carries the disease, and the new insecticides such as D.D.T. and Gammexane have made eradication a practical possibility by spraying areas by hand, or from aircraft, to destroy both larvæ and adult mosquitoes. Already vast and one-time dangerous areas of the globe have been rendered safe for mankind through the medium of these chemical agencies and the whole world knows of the use of D.D.T. in preventing the spread of typhoid in liberated countries after the war—notably in Italy where literally tons of D.D.T., used as powder on millions of persons and as sprays in hundreds of thousands of houses, stamped out a threatened plague in a matter of days. It would be possible to continue in this vein, giving example after example of how chemists have, in collaboration with other scientists, been responsible for protecting the health and saving the lives of untold hosts—work which chemists perform as the normal course of their duties.

Cleanliness, or sanitation, that is the control of the germs or their carriers outside the body, is the foundation of all health, whether of the individual or the populace as a whole. Chemistry helps us to maintain control over hygienic conditions so that plagues, such as were common in Biblical times and in the Middle Ages, no longer afflict us here. Purity of water supplies has materially helped in the application of hygienic measures, and the chemist is active in this sphere—the sterilisation of drinking water for example, being effected by accurately controlled chlorination so that water reaches us free of harmful bacteria. Water is softened by the addition of lime to separate out those constituents which cause hardness, whilst base-exchange processes have been developed enabling any household or commercial supply, from whatever source, to be safely and properly softened—a result which produces considerable economy in soap consumption.

During the war chemists devised a means of rendering sea-water drinkable, and many thousands of portable kits were supplied to airmen and seafarers so that, if ditched or wrecked without water supplies, sea-water could be squeezed through a bag of chemicals, the reactions of which removed the salt by an exchange process. This development saved many lives during the war, and outfits will doubtless form a standard fitting for aircraft and ships in the future.

Factory effluents, which often contain substances harmful to fish or plant life in rivers, have also been studied and can be controlled by the chemist, so that this type of plant or fish poisoning need no longer occur, and the natural power of rivers to purify themselves is enabled to operate. Unpleasant odours from such trade effluents are also removed by chemical treatment, and the maintenance of this chemical-biological control means that any new industry discharging its effluent into a river must be examined so that the proper steps can be taken to prevent damage.

Sewage disposal presents many difficulties, particularly in large towns and cities. Sewage is largely water, and in its natural state is a great danger to health. Chemical and biological means, by what is known as the activated sludge process, render the sewage odourless and safe to handle. A continuation of the process consists in digestion of the sludge at a gentle heat, when a bacterial process liberates quantities of ' sludge gas,' which is largely methane gas. This gas can be used as fuel for engines for the generation of electricity, can be compressed or liquefied for use in place of petrol for cars, or can be used in place of or to supplement town gas. In some places it is put to all three purposes, and no new sewage works of any importance is now constructed which is not equipped for this gas production. The sewage sludge left after this treatment can be used as a fertiliser or, if dried, as a fuel for burning.

It is fitting in ending this section on health, to be reminded that coal, about which so much has been written, provides us with the basis of many fine chemicals, particularly the pharmaceutical chemicals so much used in medicine and hygiene generally to heal and to alleviate suffering.

HOMES AND BUILDING

In yielding its gas, coal provides us with coke and with ashes from which ‘ breeze ’ bricks are made for building purposes. Coal therefore enters into the very structure of our homes as well as into our health and warmth.

Though coke or furnace-ash breeze bricks are more or less artificial, the common building materials derive from natural minerals and chemistry has been effective in devising means of improving the efficiency and reliability of many of these materials, but even apparently simple processes are, in fact, liable to prove complicated, and are not yet fully understood, even when the most modern chemical and physical methods of investigation are directed upon them. Brick-making, for example, has been practised since antiquity, but the chemistry of clays still presents many a knotty problem for scientific elucidation. Again, cement manufacture is an apparently simple process, but it actually calls for sustained research. Chemical studies of its exact nature lead to modifications which enable us to improve the characteristics of materials such as concrete in-so-far as quick-setting, light weight or water-proofing are concerned. Water-proofing can be effected, for instance, by the inclusion of a special clay into the concrete. On being contacted by water the clay swells and tightly fills the pores in the concrete, rendering it water-proof.

The paints, distempers, glues, varnishes and polishes of the home are, of course, products of the laboratory, whilst chemicals enter into the fire-proofing and rot-proofing of timber and fabrics. Within the home the chemists’ sphere is equally all-embracing, and fabrics can be treated to render them shrink-proof, moth-proof, water-proof, or dyed to a very wide range of attractive colours.

The careful study of old processes has resulted in the production of better materials—witness the contrast between early ‘ artificial leather ’ upholstery and the hard-wearing and attractive material of to-day.

Entirely new materials have many uses inside and outside the house. Such are plastics, new materials not found in nature, but devised in the laboratory—purely man-made products of wide application. The variety of uses to which these materials may be put is due to their useful properties of electrical insulation, light weight, resistance to water and corrosion, etc. Ease of manufacture and ease of manipulation, coupled with a good variety of colours, has allowed many necessary articles of artistic merit to be brought within the range of most incomes, the mass-production methods resulting in low prices.

Plastics are an excellent example of the ability of the chemist to make new materials to fit new requirements, but this ability is not accomplished easily ; it is the outcome of prolonged and expensive research and experimentation. Traditional materials used in the traditional manner are usually adequate in function. Using new materials in the traditional way leads at once to difficulties, often unsuspected until they arise. A basic study of the properties and characteristics of materials, new or old, is necessary before the best applications of them can be decided, for new products call for new ways of correct usage, and often these ways are difficult to define.

FUELS

The basic chemistry of all fuel is concerned with the reaction of hydrocarbons with oxygen and the chemists' part in fuel technology deals with the control of the released heat from the fuel, be it coal or oil, or electricity derived from the consumption of another fuel.

Coal is vital to the economic existence of this country, and the chemist has done much, and can do more, to ensure the best possible utilisation of our precious fuel and basic materials. Coal seams have definite chemical properties as well as physical properties and a thorough knowledge of these is necessary if cutting and mining are to be operated to the best advantage. In the cleaning and washing of coal, chemical technology is applied, whilst laboratory analysis, coupled with industrial experiment, indicates the best type of coal suitable for use in any given type of furnace. Moisture content, volatile matter content and ash residue are important factors upon which the treatment of coal for gas making and coking, steam-raising and domestic use depend. In such ways chemists have accumulated a wide knowledge of coals, with a corresponding knowledge of what kind of coal an industry needs.

Control of coal-getting is not limited to studies of coal itself. Mines are notoriously places of danger if gases or dusts are allowed to amass. To prevent this, great quantities of air are pumped into mines, the primary object being to reduce the percentage of firedamp to below the danger point of explosion. Firedamp is methane gas, the same gas that issues, as ' natural gas,' from oil wells. The gas is commercially valuable as a fuel, as an alternative to petrol, or as a source of valuable chemicals such as carbon black, formaldehyde, etc. Research is proceeding to discover a means of collecting the gas and so use it for industrial purposes, it may be by tapping the gas, where it is in sufficient amounts, before mining begins at the seam, or by finding an economical method of separating the gas from the ventilation air as it leaves the mine. This is a problem of considerable importance to the coal industry and thus to the nation.

Dust explosions in mines are countered by laying water or by scattering stone dust of particular size to dilute the coal dust should it be disturbed and exploded. In these matters chemical research not only improves the quality and quantity of output, but makes working conditions safer for the miner.

OIL

The world consumption of oil has been steadily rising for many years. There is some oil in this country, but we import the great bulk of our requirements from overseas. When first taken from the well as crude oil, it is not suitable for most modern requirements, and the complex refining processes to which it is subjected in order to prepare fuels suitable for specialised use, involves close study and chemical knowledge of the material and the means of treating it. The exhibition portrays something of the complexity attending the production, for example, of high octane fuel for modern internal combustion engines. This has necessitated chemical investigation of the fuel itself, and the process of its combustion in the engine cylinder.

Petrol, kerosene, lubricants, asphalt, waxes and chemicals can be prepared by treatments of the crude oil. Motor and aviation fuels predominate, and these have a high octane, or anti-knock value, and are usually a blend of distillation fractions of the crude oil.

The Octane Number is the percentage of *iso*-octane, mixed with *normal*-heptane, which has the same knocking characteristics as the fuel under test. Thus a fuel having an Octane Number of 70 means that its anti-knock value will be the same as that of a blend of 70 per cent. *iso*-octane and 30 per cent. *normal*-heptane. (*Iso*-octane alone is rated 100.)

High octane fuels need greater engine compression ratios, but enable us to construct lighter weight engines having lower fuel consumption. It is not generally appreciated that chemistry, in producing high octane fuels, materially affected the design, weight and cost of internal combustion engines.

Lubricating oils are also derived from crude oil, and again the chemical and physical characteristics are important. Different lubricants are needed for mechanisms so diverse as cars, trains, aeroplanes, watches, sewing machines and vacuum cleaners. The viscosity, or resistance to flow, is equally important, and as this property alters with temperature, it is important to know the extremes of operating temperature, the running speeds of the engine and the pressure between the surfaces to be lubricated—high speed, lightly loaded mechanisms need low viscosity ‘ thin ’ oils, whilst high loads and low speeds need high viscosity oil. No matter what the operating conditions, the chemist can produce a suitably constructed oil having the proper flow or viscosity and an absence of asphalt and waxes. To these oils he adds chemicals which, known as ‘ additives,’ enhance selected characteristics such as oiliness, film strength, etc. Additives such as organic amines can also help to reduce sludge formation and will reduce oxidation of the oil—both of which will cause corrosion of pistons and bearings. Other additives, like the metallic sulphonates, have a detergent or cleaning effect on the engine. Chemistry thus helps the motorist to avoid such troubles as ring sticking, piston scuffing and clogged pipe lines.

The subject of oil fuels cannot be left without reference to the fact that there is already a tendency for the demand for high quality petrol to drop—jet propulsion, for instance, calls for a cruder base oil, such as paraffin. Both natural gas, found associated with crude oil, and the oil itself, can be used to manufacture many chemicals and already in this country vast plants have been erected to make a range of chemicals which include wetting agents and soap substitutes, the latter of decided importance during the present world shortage of fats for soap manufacture. There is no doubt but that the chemist has yet a bigger part to play in this field than ever before.

TRANSPORT AND ENGINEERING

The engineering industries rely on chemistry mainly as it affects the production of fuels, lubricants, metals, paints, rubber and plastics, though almost every item of modern mechanical equipment depends to a greater or lesser extent upon the work of the chemist. To illustrate this, in the transport industry, railways use many of the special products of chemical ingenuity, from sponge rubber for seating, the heat resistant, fire-retardant paints, the coloured, hard-wearing fabrics for upholstery to the metal parts of carriages. Floor coverings, oils and greases are also chemist controlled, as is the boiler water, which is softened in enormous quantities for railway use.

On railway tracks chemical weed-killers are used to prevent unwanted plant growth that might disturb track ballast, whilst millions of wooden sleepers are chemically impregnated to protect them against fungoid growths.

In cars and aeroplanes the impact of chemistry is as ubiquitous. In aircraft, for example, some 300 to 400 parts are made of rubber, whilst as in cars, de-icing chemicals, anti-freeze compounds, luminous dials, plastic fittings, protective dopes, enamels and electro-plated fittings, all call for the application of chemistry at one or more stages of their production.

The great developments in machine design have depended above all upon advances in metallurgy, a science in which the chemist plays an increasingly important role, particularly in the control of the processes producing enormous quantities of steels to close specifications of reliable quality. Many of the chemical methods devised for the analytical control of this production are models of ingenuity and skill.

Special developments such as stainless steels, steels with hard-wearing properties, or having special electrical and magnetic properties, depend upon the chemist for production control. The chemistry of the apparently simple processes which occur in the actual refining of iron and steel are being studied in detail, so that greater efficiency will result not only in the metal produced, but in the use of fuels for smelting, the refractory materials for furnaces and, of some importance, in the utilisation of any by-products such as basic slag, which already finds application in the manufacture of fertilisers.

In metallurgy the demand for and production of stronger materials has led to a search for new applications for those materials, just as the evolution of new desiderata has led to a search for new and improved materials to fill those needs, and in this field the development of aluminium and magnesium alloys which are light, strong and resistant to corrosion, also depends upon the work of chemists in their primary extraction and in the ultimate purity of the finished metals.

War-time production of magnesium from the sea illustrates the direct development of a simple laboratory process into a factory process of a very large scale, handling millions of tons of sea water. An excess of this metal now exists and its special properties are being investigated with a view to making greater use of this.

CONCLUSION

This part of the exhibition aims at showing, by a small selection from a vast field, that chemistry enters into most aspects of our everyday life. Chemistry is only one branch of science, however, and taking the results and applications of science generally, we must admit that willy-nilly, our present way of life is possible only by science. Here have been shown only beneficient applications of science, leading to increased health, food and comfort, thanks to the co-operative efforts of scientists, engineers and industry. But scientific knowledge is neutral ; its uses can be for good or for evil—for life or for death. It is only by knowledge and understanding that the right uses of scientific discoveries can be chosen, and it is up to all of us to make this choice.

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APPENDIX

The Solid State

23. The development of the goniometer for measuring interfacial angles of crystals, comprising : (*a*) Miller hand goniometer ; (*b*) Miller two-circle goniometer ; and (*c*) Herbert Smith three-circle goniometer.
24. Barlow models illustrating methods of filling three-dimensional space with similar, regular polyhedra.
25. Pope-Barlow models illustrating packing of unequal spheres.
26. Barlow space-group model and Astbury-Yardley tables.
27. Wollaston's cabinet with models illustrating Häuy's theory of crystal structure.
28. Sets of Tutton salts. [$X'_2(S,Se)O_4$ and $X'_2Y''(S,Se)O_4 6.H_2O$].
29. Bragg ionisation spectrometer with X-ray tube.
30. Description of methods of crystal structure determination.
31. Early structure models, including : (*a*) Rocksalt ; (*b*) Iron pyrites ; (*c*) Graphite ; and (*d*) Diamond.
32. Contour model of the experimentally determined electron density distribution in anthracene.
33. Exhibit illustrating atomic sizes and the packing of ions in crystals with structure models showing arrangement of co-ordination polyhedra.
34. The derivation of the structure of beryl.
35. Crystal structure models of some simple inorganic compounds, including : (*a*) Phosphorus pentachloride ; (*b*) Apatite ; and (*c*) Braggite.
36. Models illustrating the methods of packing SiO_4-tetrahedra.

37. Crystal structure models of some silicates, comprising: (*a*) Olivine; (*b*) Diopside; (*c*) Mica; and (*d*) Felspar; as well as that of quartz.

38. Crystal structure models of some hydrates and some more complex salts, including: (*a*) Copper sulphate pentahydrate; (*b*) Gypsum; (*c*) Alum; (*d*) Strontium azide; (*e*) Potassium amido-sulphonate.

39. Crystal structure models of Rochelle salt and pentaerythritol tetranitrate.

40. Crystal structure models of some aromatic derivatives, including: (*a*) Hexamethylbenzene; (*b*) *p*-di-Nitrobenzene; (*c*) Phthalocyanin; (*d*) Isatin; (*e*) Coronene.

41. Diagrams showing Fourier projections and other illustrations of crystal structures.

42. Crystal structure models of two organic molecular compounds.

43. The crystal structure of cellulose.

44. The crystal structure of some synthetic fibre-forming polymers.

45. Crystal structure models of geranylamine hydrochloride, β-gutta-percha and rubber.

46. The crystal structures of glucosamine hydrochloride and sucrose sodium bromide.

47. Crystal structure model of sodium penicillin.

48. Models and diagrams illustrating the interpretation of the structure of crystalline proteins: (*a*) Insulin; (*b*) Hæmoglobin.

49. Specimens, models, diagrams illustrating the properties of plant viruses.

50. The elucidation of fibre structures by W. T. Astbury.

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